DYNAMIC AND STEADY-STATE BIFURCATION FOR MODELING CHEMICAL REACTION SYSTEMS

Thesis by
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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1984

(Submitted November 9, 1983)

Dedicated to Vivian

Acknowledgement

I would like to express my special thanks to my advisor Dr. James Bailey for his advice, support and continuous encouragement throughout this work. I would also like to thank deeply Dr. Boguslaw Kuszta, whose endless and invaluable discussions with me, helped me broaden my background and viewpoints. My special thanks to Kathy Lewis and April Olson for the painstaking job of typing this thesis. Finally I would also like to thank the National Science Foundation for the financial support of this work, and the California Institute of Technology, as a whole, for providing me with an ideal academic environment.

ABSTRACT

Chemical reaction systems often exhibit nonlinear dynamic phenomena such as multiple steady states and different types of nonlinear oscillations. Furthermore, nonlinear dynamic models are essential for control and input optimization of chemical reactors. Methods of bifurcation theory are used for analysis of the nonlinear behavior of chemical reaction systems and for chemical reactor model discrimination and identification. The latter objective is attained by forcing"tame" chemical systems to bifurcate and provide valuable information about the nonlinear system nature. Discrimination between rival kinetic models is demonstrated and a strategy for accurate parameter estimation is developed. The problem of steady-state bifurcation to multiple steady states in the event that the original model equations are not reducible to a single algebraic equation is attacked using the simple geometrical method of Newton Polyhedra. This method is particularly useful for analysis of feedback induced steady-state bifurcations.The theory of normal forms is used to illustrate that systems when close to bifurcation exhibit even locally their nonlinear characteristics. The most common types of bifurcation phenomena are discussed and the minimum number of

feedback (or system) parameters that must be varied to attain the various bifurcational structures is determined. Systems that are easily reducible to normal forms (simpler locally equivalent polynomial systems) are identified with distinctive advantages for the study of steady state and eigenvalue structure close to bifurcation. The analogy between some chemical systems and a particle's motion in a potential field is exploited to gain special insights into the chemical systems' dynamics. Chemical examples include nitrous oxide decomposition on NiO catalyst, consecutive-competitive reaction systems in a CSTR, parallel nonisothermal reactions of arbitrary order in a CSTR, reactions between adsorbed chemical species, coupled oscillating autocatalytic CSTRs and a class of feedback regulated enzymatic reaction systems.

TABLE OF CONTENTS

Chapter 1: Introduction

Motivation and Background

Modeling chemical reaction systems is essential for process design, optimization and control. The models that describe chemical systems are usually nonlinear since they involve nonlinear rate expressions. The nonlinearities in the rate expressions arise due either to making certain hypotheses (e.g. quasi-steady state or fast equilibrium [1]), or simply because most elementary reaction step rates depend on more than one chemical species concentration in a nonlinear fashion. The nonlinear nature of most reaction systems is responsible for different phenomena, such as steady-state multiplicity as well as periodic and more complicated types of oscillations [e.g. 2-10]. In order to model appropriately and to predict such phenomena, one must develop nonlinear dynamic models.

Unsteady-state models are necessary both for control and optimization purposes. Obtaining overall rate expressions from fitting steady-state data and using them in dynamic models (which are subsequently linearized to be used for control) is very often unjustified and may lead to very serious problems. In many catalytic reaction systems the reaction steps that involve surface species may be slow enough that quasi-steady state or fast equilibrium hypotheses are totally unreasonable. In such circumstances one has to assume elementary reaction step mechanisms and obtain mass and possibly (in nonisothermal cases) energy balances for each chemical species both in the gas phase and on the catalytic surface. Furthermore, one may not always safely linearize the obtained nonlinear dynamic models and apply classical control schemes for linear systems. Such a procedure often leads to a "runaway" from the desired operating conditions or an onset of undesirable oscillations [e.g. 11]. Consequently, in order to evaluate the possibilities that

arise upon application of a classical control scheme to a chemical reaction system, good nonlinear dynamic models should be obtained.

Nonlinear dynamic models are also essential in order to perform transient input optimizations for chemical reactors. It has been demonstrated repeatedly that unsteady inputs may enhance the overall yields or selectivities of chemical reactors [e.g. 12-16]. It has also been demonstrated that such an improvement of the overall reactor performance is due entirely to the nonlinear nature of the chemical systems [17].

The three reasons that were just outlined above indicate the significance of obtaining nonlinear dynamic models of chemical reaction systems. Making different assumptions regarding the elementary reaction step mechanisms of catalytic chemical reactions, different nonlinear dynamic models are obtained. The task then is to discriminate between the rival kinetic models and verify the validity of different assumptions. It should be emphasized that it is desirable to be able to determine the best kinetic model based only on gas phase concentration measurements since surface concentration measurements are not always easy or accessible. The idea is to use appropriate inputs to excite the slow modes of the system that are due to surface reactions and infer conclusions about these reactions indirectly. Finally, it is desirable to be able to predict, based on the obtained models, the observed dynamic behaviors and to evaluate the physical factors that are responsible for such dynamics.

OBJECTIVES AND THESIS OUTLINE

It has been suggested in the past that the presence of exotic dynamics, such as steady-state multiplicities and self-sustained oscillations, may be used for rival kinetic model discrimination [7]. However, most chemical systems are "tame" in

the sense that they possess a unique stable steady state for all inputs and do not exhibit "exotic" dynamics. In such circumstances one has to excite the system, forcing it to bifurcate by artificially introducing multivariable feedback control. Traditionally, feedback is used to control a chemical reaction system at a certain operating steady state (set point).

The suggestion here is to use multivariable feedback control to destabilize the system steady state, and draw conclusions about its nonlinear nature by observing the induced dynamic behavior. In a feedback scheme the input to a chemical reactor will be manipulated continuously according to concentration (or other output characteristic) measurements at the effluent. Although the approach is sufficiently general to be used for any physical system, this work will be concentrated on lumped chemical reaction systems. The dynamics of such systems are described by

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x},\mathbf{u},\mathbf{b},\mathbf{k}) \tag{1}$$

where $\mathbf{x}$ is a state vector of species concentrations, $\mathbf{u}$ is the reactor input, $\mathbf{b}$ is a vector of feedback parameters, and $\mathbf{k}$ is a vector of system parameters such as rate constants.

Nonlinear systems of form (1) with freely adjustable parameters are best analyzed using the methods of modern bifurcation theory. Bifurcation is understood as the loss of stability of a steady state of system (1) with appearance of new stable attracting states, either steady or oscillatory, as a system parameter is varied. Since nondegenerate linear systems' trajectories generally go either to the single stationary point (steady state) or to infinity (if the steady state is unstable), bifurcation to other stable attracting states is a nonlinear system characteristic. The major objective of this thesis is to use results of bifurcation theory to organize an analysis of the possible dynamics of lumped chemical systems of the form of Eqn. (1). The application of multivariable control feedback to force chemical sys-

tems to bifurcate will be explored in detail, in order to develop a general method for model discrimination and parameter estimation. In parallel, for the cases in which nonlinear dynamic behavior is observed in chemical reaction models for systems with steady inputs, bifurcation analysis will provide an insight into how "exotic" dynamics are created as well as which physical parameters (or combinations thereof) are responsible for these nonlinear dynamics. Also, the values of parameter combinations which provide exotic dynamics are characterized.

In Chapter 2, discrimination between rival kinetic models using multivariable control feedback is investigated. The problem of finding a general strategy for accurate determination of unknown model parameters (k) is considered.

Chapter 3 deals with the problem of steady-state bifurcation which is the most common type of bifurcation and is usually brought about by variation of a single feedback parameter. Steady-state bifurcation for systems that are reduced easily to a single algebraic equation has been analyzed elsewhere [18]. In this chapter the problem is considered for systems that are reducible to a few nonlinear algebraic equations, with further reduction being impossible or impractical.

In Chapter 4 the different possible dynamic phenomena that arise via bifurcation from a steady state are examined. Methods to determine the number of feedback (or physical) parameters to induce different types of bifurcational structures are developed. The possibility of using the theory of normal forms (locally equivalent much simpler forms) to gain some insight into why a system's nonlinearity is best manifested close to bifurcation and to predict possible dynamic behaviors is explored.

In general, reduction of a system to normal form is very difficult. In Chapter 5 a general class of systems that are reducible to a special type of normal form via a simple affine transformation that retains steady state and eigenvalue structure is

identified. The normal form parameters are then given explicitly as functions of the original system parameters, and the analysis of the more complicated original systems is performed easily by considering the dynamics of much simpler systems.

Finally, in Chapter 6, analysis of certain chemical systems' dynamics is pursued by considering a mechanical analog of particle motion in a potential field. Global stability characteristics and special insights that arise from this analogy are explored.

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CHAPTER 2 : DISCRIMINATION AND IDENTIFICATION OF DYNAMIC CATALYTIC REACTION MODELS VIA INTRODUCTION OF FEEDBACK

INTRODUCTION

It is well known that catalytic reaction systems may be modeled in several different ways all of which are consistent with laboratory steady-state measurements [1]. On many occasions some of the models may be excluded based upon spectroscopic data. There are cases, however, in which current chemical methods alone are unable to discriminate between rival models. In such instances dynamic studies provide a useful tool. Furthermore, numerous recent experimental studies have shown that transients in fluid-catalyst interactions, involving slow steps on or near the catalyst surface, can significantly influence the overall dynamics of catalytic reactors. Determination of models for these phenomena necessitate dynamic experiments. Because of the potential importance of nonlinear transient phenomena for reactor design, optimization, and control, it is desirable that these dynamic experiments and the models deduced from them encompass the major nonlinear characteristics of the catalytic reaction.

Such motivations have inspired many researchers to base their modeling on transient experiments. Reviews by Bennett [1] and Kobayashi and Kobayashi [2] summarize the so-called "transient response" method. In this method, transient responses of catalytic reactions to step-up/step-down perturbations in feed concentrations are used to discriminate between alternative models and identify parameters such as kinetic constants. However, such transient data may agree closely for several candidate models making discrimination impossible. In a recent study by M. Kobayashi of CO oxidation on a silver catalyst, several different parameters sets were found to give the same fit to transient data [3]. Also, such step experiments do not impose the most sensitive and

rigorous test of nonlinear transient kinetic models. It is the purpose of this paper to introduce an alternative method of model discrimination, verification and identification.

As Andronov and Chaikin point out [4], the most fundamental dynamic property of a nonlinear system is the existence (or absence) of stable oscillatory behavior. Some chemical reaction systems are known to exhibit self-sustained oscillations [e.g., 5-15]. Usually an autocatalytic step is required. Several different model forms have been suggested in the literature in the effort to illuminate the mechanisms that lead to such self-sustained oscillations [16-20].

However, most reaction systems are sufficiently tame that they do not exhibit self-oscillations. On such occasions the system can be forced or modified such that nonlinear oscillations occur. One way to achieve this is introduction of a periodic feed. This approach is the basis of the so-called "DC-shift technique" for identifying the modes of the system [21].

An alternative identification method, first introduced here for chemical systems and in [22] for general dynamic systems, is to introduce feedback based on concentration measurements. Positive feedback has been suggested before as a means of creating stable autonomous oscillations in a closed-loop reactor-controller system for the purpose of improving time-average reactor performance [23]. The emphasis here is utilization of feedback-induced oscillations for model discrimination and identification.

The major advantage of this method is that very important nonlinear information is accessible only when the system is close to bifurcation. Systems not close to bifurcation are termed "hyperbolic", and for such systems there exists a nonlinear transformation converting them to equivalent linear systems, much nonlinear information thus being lost or "hidden" [24]. In the next

section the mathematical background used in this work is introduced. Next, the theory is applied to an example reaction system, the decomposition of nitrous oxide on nickel oxide catalyst. Finally the results are discussed and some general conclusions are suggested.

MATHEMATICAL BACKGROUND

Hopf Bifurcation Theory

Hopf bifurcation theory provides powerful mathematical methods for analysis of the appearance of a certain class of nonlinear oscillations [25]. The utility of this theory for chemical reactor analysis has been clearly illustrated in several previous studies of isothermal [e.g., 26-28] and nonisothermal [e.g., 29] reactors. A brief summary of certain parts of this theory is necessary here to introduce certain terms and results which are central to this work and which have not appeared previously in the chemical engineering literature.

Consider a dynamical system of the form

$$\frac{dx}{dt} = F(x,\nu) \tag{1}$$

where ν is a system parameter called the "bifurcation parameter". In the above equation x is an n-dimensional vector and F is a vector-valued function:

$$F:E^n \times E^1 \longrightarrow E^n \quad . \tag{2}$$

It is assumed that the system of Eqn. (1) has an isolated stationary point $x_s(\nu)$ and that F is analytic in x and ν in some neighborhood of (x_s,ν_c) in $E^n \times E^1$. Here ν_c is the critical value of the bifurcation parameter, to be defined next. If (i) the Jacobian matrix of F evaluated at the stationary point has a complex conjugate pair of eigenvalues λ and $\bar{\lambda}$, such that

$$\lambda(\nu) = \alpha(\nu) \pm i\omega(\nu) \tag{3.1}$$

where

$$\alpha(\nu_c) = 0 \quad ; \quad \alpha'(\nu_c) \neq 0 \quad ; \quad \omega(\nu_c) \triangleq \omega_0 > 0 \quad , \tag{3.2}$$

and (ii) the remaining n-2 eigenvalues of the Jacobian have negative real parts, then system (1) has a family of periodic solutions. Eqns. (3.1) and (3.2) define ν_c; it is a value of ν for which a pair of complex eigenvalues of the system Jacobian crosses the imaginary axis.

If conditions (i) and (ii) are satisfied, it also follows that there exists a scalar ε_H and an analytic function

$$\mu^H(\varepsilon) = \sum_{i=2}^{\infty} \mu_i^H \varepsilon^i + \nu_c \quad ; \quad 0 < \varepsilon < \varepsilon_H \quad , \tag{4}$$

such that for each ε in $(0,\varepsilon_H)$ there exists a periodic solution $P_\varepsilon(t)$ occurring for $\nu = \mu^H(\varepsilon)$. The period $T^H(\varepsilon)$ of $P_\varepsilon(t)$ is an analytic function which may be written

$$T^H(\varepsilon) = \frac{2\pi}{\omega_0}\left[1 + \sum_{i=2}^{\infty} \tau_i^H \varepsilon^i\right] \quad ; \quad 0 < \varepsilon < \varepsilon_H \quad . \tag{5}$$

Exactly two of the Floquet exponents approach 0 as ε does. One is zero and the other is an analytic function.

$$\beta^H(\varepsilon) = \sum_{i=2}^{\infty} \beta_i^H \varepsilon^i \quad ; \quad 0 < \varepsilon < \varepsilon_H \quad . \tag{6}$$

The periodic solution is orbitally asymptotically stable if $\beta^H(\varepsilon) < 0$.

Hassard, Kazarinoff and Wan [25] analyze the steps that must be followed to evaluate the leading coefficients μ_2, τ_2 and β_2 in the expansions (4), (5) and (6), respectively. They also provide a numerical "bifurcation package" that finds the critical point, gives eigenvalues and eigenvectors at (x_s,ν_c), and provides values for the coefficients μ_2, τ_2 and β_2. The procedure involves

transformation of the original system of differential equations to the Poincaré normal form (a topologically equivalent system with as simple form as possible) and subsequent reduction of the system to the central manifold (a two-dimensional local patch of surface that contains all the relevant information of the n-dimensional system near the bifurcation point) [25,30].

Steady State Multiplicity

The modification of a dynamic system by introduction of feedback may result in addition of otherwise nonexistent steady-state multiplicity. Steady-state multiplicity has repeatedly been observed and predicted in chemical reactor systems [e.g., 31]. Bifurcation of steady-state equilibria may be treated using some results from singularity theory [31,32].

Let the scalar-valued function $G(q,\eta)$ be defined on Ω in E^2. Suppose also that none of the following set of equations are satisfied at any point in Ω:

(i) $$G_{\eta\eta} = 0 \quad ; \tag{7}$$

(ii) $$G = G_q = G_{qq} = G_{qqq} = 0 \quad ; \text{ and} \tag{8}$$

(iii) $$G = G_q = G_\eta = G_{q\eta}^2 - G_{qq}G_{\eta\eta}$$
$$= G_{qqq}v^3 + 3G_{qq\eta}v_q^2v_\eta + 3G_{q\eta\eta}v_qv_\eta^2 + G_{\eta\eta\eta}v_\eta^3 = 0 \tag{9.1}$$

for all $(v_q,v_\eta) \neq 0$ for which

$$G_{qq}v_q^2 + 2G_{q\eta}v_qv_\eta + G_{\eta\eta}v_\eta^2 = 0 \quad . \tag{9.2}$$

Then at any point (q_0,η_0) in Ω for which $G(q_0,\eta_0) = 0$, the local nature of the bifurcation diagram $\{G = 0\}$ is described by one of the eight singularities in Table 1 [32].

Decrement Diagrams

It will be necessary below to examine the influences of changes in multiple parameters on reactor system dynamics. Decrement diagrams are especially convenient for this analysis. Consider a family A of linear differential operators in a Euclidean space E^n, depending smoothly on a parameter vector $\mu \in M$, where M is a given parameter space in E^p,

$$A(\mu): E^n \to E^n \tag{10}$$

Definition [33]: The increment of the family A is defined as being that function h of the parameters, the value of which at μ is the greatest real part of all eigenvalues of the operator $A(\mu)$:

$$h(\mu) = \lim_{t \to \infty} \frac{1}{t} \ln \| e^{A(\mu)t} \| \tag{11}$$

The function h is continuous but not necessarily differentiable. The family of level curves of h in M ($M \equiv E^2$ will be considered here) is called the *decrement diagram*. The whole parameter plane can be stratified as follows:

CODIMENSION 0 REGIME: almost all points on the parameter space (up to a set of measure zero) belong in this regime (two-dimensional regions of space). There are two possibilities:

i) Stratum D_1: the maximal real part belongs to a single real eigenvalue;

ii) Stratum D_2: the maximal real part belongs to a complex conjugate eigenvalue pair.

CODIMENSION 1 REGIME: these are curves on the parameter plane. Three possibilities exist:

i) Stratum F_1: the maximal real part belongs to two coincidental real eigenvalues which correspond to a 2x2 Jordan block.

ii) Stratum F_2: the maximal real part belongs to three eigenvalues, one real and a complex conjugate pair.

iii) Stratum F_3: the maximal real part belongs to two distinct complex conjugate pairs.

CODIMENSION 2 REGIME: these are points on the parameter plane. Five possibilities exist:

i) Stratum G_1: the maximal real part belongs to three real eigenvalues corresponding to a 3x3 Jordan block.

ii) Stratum G_2: the maximal real part belongs to four eigenvalues, two coincident complex conjugate pairs corresponding to two identical 2x2 Jordan blocks.

iii) Stratum G_3: the maximal real part belongs to four eigenvalues, two of which are real and coincident and correspond to a 2x2 Jordan block; the other two are complex conjugate.

iv) Stratum G_4: the maximal real part belongs to five eigenvalues: one real and two distinct complex conjugate pairs.

v) Stratum G_5: the maximal real part belongs to three distinct complex conjugate pairs.

Segments F_1 and F_2 divide M into D_1 and D_2 regions. At the intersection of F_1 and F_2 there is always a G_1 point. Other G_i points lie at the intersection of F_i segments.

Now the stability boundary can be described as the curve(s) in M along which the maximal real part of the eigenvalues of A (here the Jacobian matrix corresponding to nonlinear system (1)) is zero (zero increment). A change in

parameter values which results in crossing of the stability boundary in the D_1 region means simple loss of stability. All system trajectories escape from the neighborhood of the stationary point x_s. Crossing of the stability boundary in the D_2 region means Hopf bifurcation. Loss of stability in an F_i region results in a higher order bifurcation and is possible only at finite number of isolated points. Finally, loss of stability in a G_i region is improbable for a two-parameter system and not generic (a small shift in any parameter eliminates it.)

It can be proven [35] that along the stability boundary in the D_1 region, a bifurcating branch of steady-states appears and exchange of stability is observed. Thus a line of steady-state multiplicity in E^2 must coincide with the stability boundary in the D_1 region. As a result, the points at which F type bifurcation occurs must lie on the lines along which steady-state multiplicity appears.

REACTION MODEL DISCRIMINATION VIA THE FEEDBACK APPROACH

For isothermal, isobaric reactions in a catalytic CSTR, the transient material balances have the form:

$$\frac{dc}{dt} = \frac{1}{\tilde{t}_R}(c_f - c) + r_f(c, c_s) \tag{12.1}$$

$$\frac{dc_s}{dt} = r_g(c, c_s) \tag{12.2}$$

where c and c_s are q- and s-dimensional state vectors denoting the gas phase and surface species concentrations, respectively, and r_f, r_g are vector functions of c and c_s denoting the net rates of formation of gas phase and surface species, respectively. $\tilde{t}_R$ is the reactor mean residence time. If the feed concentration is manipulated in response to the effluent concentrations measurement according to:

$$c_f(t) = \hat{F}(c(t),\nu), \tag{13}$$

ν being some vector of feedback parameters, then the closed loop dynamics are described by:

$$\frac{dc}{dt} = \frac{1}{\tau_R}(\hat{F}(c,\nu) - c) + r_f(c,c_s) \tag{14.1}$$

$$\frac{dc_s}{dt} = r_g(c,c_s) \tag{14.2}$$

which is of the form (1). Since the above model is a result of an assumed elementary reaction step mechanism, the functions r_f and r_g are polynomials, usually of degree less than or equal to three if mass action kinetics are assumed. Thus, all the smoothness conditions required for the R.H.S. of Equation (1) are met, and the theory summarized above applies.

Yang, Cutlip and Bennett [34] have studied the decomposition reaction of nitrous oxide to oxygen and nitrogen over nickel oxide catalyst. The overall reaction may be written as:

$$2N_2O \longrightarrow 2N_2 + O_2 \tag{15}$$

As indicated by Yang *et al.*, two alternative elementary reaction sequences for this reaction have been suggested in the literature:

MECHANISM I:

$$N_2O + S \xrightarrow{k_1} N_2 + OS$$
$$2OS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_2 + 2S \tag{16}$$

MECHANISM II:

$$N_2O + S \xrightarrow{k_1'} N_2 + OS$$
$$N_2O + OS \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} N_2 + O_2 + S \tag{17}$$

where S and OS denote the catalytic sites and the adsorbed oxygen species, respectively.

Yang *et al.* assumed that the first mechanism is the correct one and that mass action kinetics apply. Thus the first reaction rate may be expressed as:

$$r_1 = k_1 c_{So}(1-\theta) c_{N_2O} \tag{18}$$

and the second reaction rate as

$$r_2 = k_2 (c_{So}\theta)^2 - k_{-2} c_{So}^2 (1-\theta)^2 c_{O_2} \tag{19}$$

where by c_{N_2O}, c_{O_2} and c_{N_2} are denoted the concentrations of N_2O, O_2 and N_2 in the reactor expressed in moles/cm^3, respectively. c_{So} stands for the maximum possible concentration of adsorbed oxygen atoms (mole/cm^3) and θ stands for the partial surface coverage ($0 \le \theta \le 1$). In a catalytic CSTR with residence time $\bar{t}_R = 16.8$ sec. at 352°C the following values for the kinetic parameters were determined from steady-state data and step-up/step-down transient response measurements [34]:

$$k_1 = 1.367 \times 10^4 \frac{cm^3}{mole \cdot sec} \qquad k_2 = 6.438 \times 10^5 \frac{cm^3}{mole \cdot sec}$$
$$k_{-2} = 9.451 \times 10^{11} \frac{cm^6}{mole^2\ sec} \qquad c_{So} = 8.44 \times 10^{-7} \frac{mole}{cm^3\ of\ gas} . \tag{20.1}$$

Under the assumption that the flow rate of the diluent gas (argon) is very large compared to the flow rate of N_2O in the feed and that the feed does not contain N_2 nor O_2, the governing equations for the dynamic behavior of reactants and products may be written as follows:

$$\frac{dc_{N_2O}}{dt} = -k_1 c_{N_2O} c_{So}(1-\theta) - \frac{c_{N_2O} - c_{N_2O,f}}{\bar{t}_R} \tag{20.2}$$

$$\frac{dc_{N_2}}{dt} = k_1 c_{N_2O} c_{So}(1-\theta) - \frac{c_{N_2}}{\bar{t}_R} \tag{20.3}$$

$$\frac{dc_{O_2}}{dt} = k_2 c_{So}^2 \theta^2 - k_{-2} c_{So}^2 (1-\theta)^2 c_{O_2} - \frac{c_{O_2}}{\bar{t}_R} \tag{20.4}$$

$$\frac{d[c_{So}(1-\theta)]}{dt} = -k_1 c_{N_2O} c_{So}(1-\theta) + 2k_2 c_{So}^2 \theta^2 - 2k_{-2} c_{So}^2 (1-\theta)^2 c_{O_2} \tag{20.5}$$

Defining dimensionless variables:

$$\tilde{x} = \frac{c_{N_2O}}{c^0_{N_2O,f}}, \quad \tilde{y} = \frac{c_{N_2}}{c^0_{N_2O,f}}, \quad \tilde{z} = \frac{c_{O_2}}{c^0_{N_2O,f}}, \tag{20.6}$$

$$\tilde{\omega} = \frac{c_{So}(1-\theta)}{c^0_{N_2O,f}}, \quad \tilde{u} = \frac{c_{N_2O,f}}{c^0_{N_2O,f}}, \quad \tilde{t} = \frac{t}{\bar{t}_R}, \quad \tilde{\alpha} = \frac{c_{So}}{c^0_{N_2O,f}},$$

$$\tilde{\beta} = k_1 c^0_{N_2O,f} \bar{t}_R, \quad \gamma = k_2 c^0_{N_2O,f} \bar{t}_R, \quad \delta = k_{-2} c^{0\,2}_{N_2O,f} \bar{t}_R$$

the equations become:

$$\frac{d\tilde{x}}{d\tilde{t}} = -\tilde{\beta}\tilde{x}\tilde{\omega} - (\tilde{x} - \tilde{u}) \tag{21.1}$$

$$\frac{d\tilde{y}}{d\tilde{t}} = \tilde{\beta}\tilde{x}\tilde{\omega} - \tilde{y} \tag{21.2}$$

$$\frac{d\tilde{z}}{d\tilde{t}} = \gamma(\tilde{\alpha} - \tilde{\omega})^2 - \delta\tilde{\omega}^2\tilde{z} - \tilde{z} \tag{21.3}$$

$$\frac{d\tilde{\omega}}{d\tilde{t}} = -\tilde{\beta}\tilde{x}\tilde{\omega} + 2\gamma(\tilde{\alpha} - \tilde{\omega})^2 - 2\delta\tilde{\omega}^2\tilde{z} \tag{21.4}$$

Here $c^0_{N_2O,f}$ is a reference feed (concentration) chosen here to be $10^{-7}\ \frac{\text{moles}}{\text{cm}^3}$.

The parameters $\tilde{\alpha}, \tilde{\beta}, \gamma, \delta$, then, have the values:

$\tilde{\alpha} = 8.44$, $\tilde{\beta} = 0.0230$, $\gamma = 1.0816$, $\delta = 0.1588$

Assuming mass action kinetics, the reaction rates for mechanism II are

$$r_1' = k_1' c_{So}' (1-\theta) c_{N_2O} \tag{22}$$

$$r_2' = k_2' c_{N_2O} c_{So}' \theta - k_{-2}' c_{N_2} c_{O_2} c_{So}' (1-\theta) \tag{23}$$

Then the dynamic equations for this model become

$$\frac{dc_{N_2O}}{dt} = -k_1' c_{So}' (1-\theta) c_{N_2O} - k_2' c_{N_2O} c_{So}' \theta + k_{-2}' c_{N_2} c_{O_2} c_{So}' (1-\theta) - \frac{c_{N_2O} - c_{N_2O,f}}{\bar{t}_R} \tag{24.1}$$

$$\frac{dc_{N_2}}{dt} = k_1' c_{So}' (1-\theta) c_{N_2O} + k_2' c_{N_2O} c_{So}' \theta - k_{-2}' c_{N_2} c_{O_2} c_{So}' (1-\theta) - \frac{c_{N_2}}{\bar{t}_R} \tag{24.2}$$

$$\frac{dc_{O_2}}{dt} = k_2' c_{N_2O} c_{So}' \theta - k_{-2}' c_{N_2} c_{O_2} c_{So}' (1-\theta) - \frac{c_{O_2}}{\bar{t}_R} \tag{24.3}$$

$$\frac{d[c_{So}' (1-\theta)]}{dt} = -k_1' c_{So}' (1-\theta) c_{N_2O} + k_2' c_{N_2O} c_{So}' \theta - k_{-2}' c_{N_2} c_{O_2} c_{So}' (1-\theta). \tag{24.4}$$

Defining dimensionless variables as before (see Nomenclature), Eqns. (24) may be rewritten:

$$\frac{d\tilde{x}}{d\tilde{t}} = -\beta' \tilde{x} \tilde{\omega} - \gamma' \tilde{x} (\alpha' - \tilde{\omega}) + \delta' \tilde{\gamma} \tilde{z} \tilde{\omega} - (\tilde{x} - \tilde{u}) \tag{25.1}$$

$$\frac{d\tilde{y}}{d\tilde{t}} = \beta'\tilde{x}\tilde{\omega} + \gamma'\tilde{x}(\alpha' - \tilde{\omega}) - \delta'\tilde{y}\tilde{z}\tilde{\omega} - \tilde{y} \tag{25.2}$$

$$\frac{d\tilde{z}}{d\tilde{t}} = \gamma'\tilde{x}(\alpha' - \tilde{\omega}) - \delta'\tilde{y}\tilde{z}\tilde{\omega} - \tilde{z} \tag{25.3}$$

$$\frac{d\tilde{\omega}}{d\tilde{t}} = -\beta'\tilde{x}\tilde{\omega} + \gamma'\tilde{x}(\alpha' - \tilde{\omega}) - \delta'\tilde{y}\tilde{z}\tilde{\omega} \tag{25.4}$$

Yang *et al.*[34] have shown that the Mechanism I model with the parameters given above fits well steady-state and step-up/step-down transient experimental data. This model can therefore be used here as a basis for testing the consistency of the Mechanism II model with such data. Consequently, the following question will be explored first: with appropriate choice of Mechanism II model parameters, to what degree can this model reproduce the steady-state and transient responses provided by the Mechanism I? After this, with parameters so fixed in both models, the behavior of these different models in the presence of linear and nonlinear feedback is analyzed and compared.

Using the model for Mechanism I, steady-state effluent concentration values have been calculated for a whole range of feed concentrations $\tilde{u}$. Then a least squares algorithm has been used to calculate values of the parameters of the second model to obtain the best fit to the steady-state values predicted by model I. For the parameter values

$\alpha' = 8.4275$, $\beta' = 0.0115$, $\gamma' = 0.2255$, $\delta' = 0.9719$,

the correlation is found to be excellent. In Table 2, the calculated steady-state values are presented for both models as a function of feed concentration. The values of only one gas phase species concentration are given since the other concentrations are easily found by stoichiometry. Clearly, the two models are indistinguishable in this comparison based on steady-state properties.

Next, the transient responses are simulated for each model. The initial conditions are the steady-state concentrations corresponding to $\tilde{u} = 1$. For $\tilde{t} > 0$, $\tilde{u}$ is fixed at the different value $\tilde{u} = 1.5$. The model equations have been integrated numerically using Runge-Kutta-Gill with Adams-Moulton predictor-corrector (MODDEQ), and $\tilde{x}$, $\tilde{y}$ and $\tilde{z}$ have been plotted as a function of $\tilde{t}$ (Fig. 1). It is clear that the transient response is quite similar for both models, especially for $\tilde{x}$ and $\tilde{y}$. Thus discrimination is difficult using this method for this example.

For both models with the parameters given above, all steady states are locally asymptotically stable; in other words, all of the Jacobian eigenvalues at all steady states have negative real parts. Simulations starting arbitrarily far from the steady state show monotonic return to this steady state and hence indicate absence of self-sustained oscillations for both models.

Consequently, the influence of an external feedback is considered. It will be assumed that the concentration of nitrous oxide in the feed is manipulated according to continuous measurements of gas phase concentrations in the effluent so that

$$\tilde{u} = \tilde{u}_s + \tilde{F}(\tilde{x} - \tilde{x}_s, \tilde{y} - \tilde{y}_s, \tilde{z} - \tilde{z}_s) \qquad (26)$$

where $\tilde{x}_s$, $\tilde{y}_s$ and $\tilde{z}_s$ are the steady-state values corresponding to $\tilde{u} = \tilde{u}_s$. Henceforth the values $\tilde{u}_s$, $\tilde{x}_s$, $\tilde{y}_s$ and $\tilde{z}_s$ will be called the reference steady-state values of these dimensionless concentrations. The value of $\tilde{u}_s$ will be taken here to be unity.

Introduction of feedback may in general change the steady-state morphology. Clearly by requiring that $\tilde{F}(0,0,0) = 0$ in Eqn. (26), the reference steady state is also a steady state of the closed loop system. However, additional steady states may appear in the closed-loop system. Also, as mentioned earlier, feedback may change the dynamic behavior of the system significantly, possibly

introducing bifurcations which change the qualitative dynamic structure of the closed-loop system. After examining the effect of feedback on steady-state multiplicity, the dynamic implications of this modification of the reactor will be considered.

Steady-State Multiplicity

Proportional feedback is the simplest mathematical form and consequently will be considered first. Thus, the inlet feed concentration is manipulated according to:

$$\tilde{u} = \tilde{u}_s - b_1(\tilde{x} - \tilde{x}_s) - b_2(\tilde{y} - \tilde{y}_s) \tag{27}$$

For the Mechanism I model, setting the right-hand side of Eqn. (21) equal to zero and eliminating $\tilde{z}$ and $\tilde{w}$ gives two equations in two unknowns $\tilde{x}$ and $\tilde{y}$:

$$\tilde{f}_1(\tilde{x},\tilde{y}) = -\tilde{\beta}^2\tilde{x}\tilde{y} + 2\gamma\tilde{\alpha}^2\tilde{\beta}^2\tilde{x}^2 + 2\gamma\tilde{y}^2 - 4\tilde{\alpha}\tilde{\beta}\gamma\tilde{x}\tilde{y} - \delta\tilde{y}^3 = 0 \tag{28}$$

$$\tilde{f}_2(\tilde{x},\tilde{y},\tilde{u}) = \tilde{x} + \tilde{y} - \tilde{u} = 0 \tag{29}$$

Substituting for $\tilde{u}$ using Eqn. (27) and eliminating $\tilde{y}$ from the resulting equations yields one equation in $\tilde{x}$:

$$\begin{aligned}\tilde{G}(\tilde{x}) = {} & (-\tilde{\beta}^2 - 4\tilde{\alpha}\tilde{\beta}\gamma)\tilde{x}\left(\frac{\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}}{1+b_2}\right) + 2\gamma\tilde{\alpha}^2\tilde{\beta}^2\tilde{x}^2 \\ & + 2\gamma\left(\frac{\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}}{1+b_2}\right)^2 \\ & - \delta\left(\frac{\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}}{1+b_2}\right)^3 = 0\end{aligned} \tag{30}$$

It is readily verified that positive solutions of Eqn. (30) near the reference steady-state value $\tilde{x}_s$ imply positive values of $\tilde{y}$, $\tilde{z}$, and $\tilde{w}$.

From this equation one obtains:

$$\tilde{G}_{\tilde{x}}(\tilde{x}) = \frac{(-\tilde{\beta}^2 - 4\tilde{\alpha}\tilde{\varepsilon}\gamma)}{1+b_2}\left(\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - 2(1+b_1)\tilde{x}\right) + 4\gamma\tilde{\alpha}^2\tilde{\beta}^2\tilde{x}$$

$$- 4\gamma(1+b_1)\frac{\left(\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}\right)}{(1+b_2)^2}$$

$$+ \frac{3\delta(1+b_1)}{(1+b_2)^3}\left(\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}\right)^2 \qquad (31)$$

and

$$\tilde{G}_{\tilde{x}\tilde{x}}(\tilde{x}) = \frac{2(1+b_1)(\tilde{\beta}^2 + 4\tilde{\alpha}\tilde{\varepsilon}\gamma)}{1+b_2} + 4\gamma\tilde{\alpha}^2\tilde{\beta}^2 + \frac{4\gamma(1+b_1)^2}{(1+b_2)^2}$$

$$- \frac{6\delta(1+b_1)^2}{(1+b_2)^3}\left(\tilde{u}_s + b_1\tilde{x}_s + b_2\tilde{y}_s - (1+b_1)\tilde{x}\right) \qquad (32)$$

Also

$$\tilde{G}_{\tilde{x}\tilde{x}\tilde{x}} = \frac{6\delta(1+b_1)^3}{(1+b_2)^3} \qquad (33)$$

Evaluating $\tilde{G}_{\tilde{x}}(\tilde{x}_s)$ and setting this equal to zero, a condition on the parameter values b_1 and b_2 is obtained:

$$b_2 = -5.9783b_1 - 6.9783 \qquad (34)$$

Evaluation of $\tilde{G}_{\tilde{x}\tilde{x}}(\tilde{x}_s)$ and substitution for b_2 using Eqn. (34) shows that $\tilde{G}_{\tilde{x}\tilde{x}}(\tilde{x}_s)$ is zero whenever $\tilde{G}_{\tilde{x}}(\tilde{x}_s)$ is zero; i.e., whenever Eqn. (34) applies. Also, as is evident from Eqn. (33), $\tilde{G}_{\tilde{x}\tilde{x}\tilde{x}}(\tilde{x}_s)$ is nonzero. Similarly, it can be shown that the remaining parts of conditions (7) to (9) are satisfied.

Evaluation of $\tilde{G}_{b_2}(\tilde{x}_s)$ shows that this partial derivative vanishes while $\tilde{G}_{xb_2}(\tilde{x}_s)$ may be readily shown to be different than zero. Thus the catastrophe depicted in Case (7) of Table 1 occurs along the line in the (b_1,b_2) parameter space defined by Eqn. (34). Plotting $\tilde{G}$ as a function of x shows that if b_2 is less than the RHS of Eqn. (34), there are three steady states which collapse along the line of Eqn. (34). Similar treatment of the steady state model for Mechanism II shows that the locus for transition from single to multiple steady states is given by

$$b_2 = -5.9847b_1 - 6.9847 \tag{35}$$

Thus the steady-state multiplicity picture is almost identical for the two models.

For reasons that will become apparent in investigation of the dynamic behavior of the closed-loop reactor system, a specific form of nonlinear feedback has been also considered, namely

$$\tilde{u} = \tilde{u}_s\left\{1 - \frac{1}{\pi}\tan^{-1}\left[b_1(\tilde{x} - \tilde{x}_s)\right] - \frac{1}{\pi}\tan^{-1}\left[b_2(\tilde{y} - \tilde{y}_s)\right]\right\} \tag{36}$$

This form of nonlinear feedback was selected because (i) it is a simple function which gives bounded u values (between zero and $2\tilde{u}_s$), a physically important and realistic property, and because (ii) it is analytic allowing application of the theory outlined above.

First, the effect of this type of feedback on steady-state multiplicity of the closed-loop system is considered. Eqns. (28) and (29) in this case become:

$$\tilde{f}_1'(\tilde{x},\tilde{y}) = -\tilde{\beta}^2\tilde{x}\tilde{y} + 2\gamma\alpha^2\tilde{\beta}^2\tilde{x}^2 + 2\gamma\tilde{y}^2 - 4\alpha\tilde{\beta}\gamma\tilde{x}\tilde{y} - 6\tilde{y}^3 = 0 \tag{37}$$

$$\tilde{f}_2'(\tilde{x},\tilde{y}) = \tilde{x} + \tilde{y} - \tilde{u}_s\left\{1 - \frac{1}{\pi}\tan^{-1}\left[b_1(\tilde{x} - \tilde{x}_s)\right] - \frac{1}{\pi}\tan^{-1}\left[b_2(\tilde{y} - \tilde{y}_s)\right]\right\} = 0 \tag{38}$$

Here $\tilde{y}$ cannot be easily eliminated to obtain one equation in $\tilde{x}$. Still it is known that a necessary condition for steady-state multiplicity is [35]:

$$\left.\frac{\partial \tilde{f}_1}{\partial \tilde{x}}\right|_{(\tilde{x}_s,\tilde{y}_s)} \cdot \left.\frac{\partial \tilde{f}_2}{\partial \tilde{y}}\right|_{(\tilde{x}_s,\tilde{y}_s)} - \left.\frac{\partial \tilde{f}_1}{\partial \tilde{y}}\right|_{(\tilde{x}_s,\tilde{y}_s)} \cdot \left.\frac{\partial \tilde{f}_2}{\partial \tilde{x}}\right|_{(\tilde{x}_s,\tilde{y}_s)} = 0 \qquad (39)$$

This condition provides the relationship that b_1 and b_2 must satify at the point of multiplicity. Condition (39) gives:

$$\frac{b_2}{\pi} = -5.9783\frac{b_1}{\pi} - 6.9783 \qquad (40)$$

for the Mechanism I model, and

$$\frac{b_2}{\pi} = -5.9847\frac{b_1}{\pi} - 6.9847 \qquad (41)$$

for the Mechanism II model. The only difference between Eqns. (40), (41) and (34), (35), respectively, is the $1/\pi$ factor which is introduced to normalize the inverse tangent functions. Numerical solution of the steady-state Eqns. (37) and (38) show the existence of three steady states below the curves defined by Eqns. (40) and (41) which collapse into one along those curves. The resemblance of the behavior in the case of the inverse tangent feedbacks to that of the proportional feedbacks is not surprising since the former function resembles the latter in the limit as their arguments go to zero ($\tan^{-1}x \sim x$ as $x \longrightarrow 0$).

Periodic Solutions

When the feed concentration is manipulated according to Eqn. (27) for linear feedback or Eqn. (36) for nonlinear feedback, values of the feedback parameters b_1 and b_2 are sought such that bifurcation to periodic solutions occurs. The eigenvalues of the Jacobian for the case of linear feedback are the same as for nonlinear feedback after taking into account the normalizing factor of $1/\pi$ for the latter case.

Decrement diagrams have been constructed for the case of inverse tangent feedback (Eqn. (38)) for both reaction models (Figs. 2 and 3). In each case, there are F_1 and F_2 curves dividing the parameter space into D_1 and D_2 regions. The stability boundary is also shown in this b_1-b_2 parameter space for both models by a dashed line.

No periodic solutions are anticipated when a single feedback is used (b_1 or b_2 zero). This can also be verified using the Routh criterion [36]. For the Model I there is a G_1 point at ($b_1 = -7.5$, $b_2 = 22.4$). Hopf bifurcation is realized at loss of stability in the D_2 region and is possible when $-7.5 < b_1 < -6.88$, $b_2 > 22.4$. For $b_2 < 22.4$ loss of stability can occur in the D_1 region. As mentioned earlier the stability line in the D_1 region coincides with the steady-state multiplicity line. Hence exchange of stabilit occurs in bifurcations to steady-state multiplicity in this region. To the left of this line, the reference steady-state becomes unstable while the two appearing steady-states are both stable.

There is one single point B at which the stability boundary crosses the F_1 line, and at this point F_1 bifurcation occurs (Fig. 2). Thus, at point B there is a double real zero eigenvalue and the Jordan block corresponding to it has the form

$$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

Point B also lies on the line along which steady-state multiplicity changes from one to three.

The decrement diagram for Model II is significantly different from that for Model I. For Model II, the G_1 point appears at ($b_1 = -4.91$, $b_2 = 15.7$) and is located well in the stable region. For $b_1 < -4$ there is always a

value of b_2 at which stability is lost in the D_2 region (Hopf bifurcation). For $b_1 > -4$, stability is lost in the D_1 region, the stability boundary coinciding with the steady-state multiplicity line, and again there is a point D at which stability is lost along the F_1 curve. The steady-state multiplicity line passes through point D as before, and at that point an F_1 bifurcation occurs. As is evident from the decrement diagram, no periodic solutions are expected for a single feedback as no bifurcations exist along the $b_1 = 0$ or $b_2 = 0$ lines.

When multiple steady states exist, closed-loop reactor dynamics are expected to depend on the eigenvalue configuration at all steady states. Accordingly, decrement diagrams have been prepared for the additional steady states which appear following the bifurcations from one to three steady states. The steady-state multiplicity lines in Figs. 2 and 3 are retained for reference in Fig. 4, which applies for inverse tangent feedback. The dotted lines in Fig. 4 are the stability boundaries for the added steady states; the F_2 locus for the added steady states is also shown (essentially the same decrement diagram applies to both of the added steady states for this example). For feedback parameters above the dotted line, the added steady states are unstable. Regions of instability of the added steady states are significantly different for the two models, suggesting the possibility of model discrimination on this basis.

Although the decrement diagram suggests the regions of the parameter space for which periodic solutions are expected, it contains no information regarding the stability and form of these solutions. Based on the decrement diagram above, one can only predict that, close to the Hopf bifurcation curve, the oscillations (if stable) will be of the harmonic type whereas in regions far from this curve oscillations are expected to be more asymmetric.

Also, gain parameters in the neighborhood of the F_1 bifurcation point may yield oscillations differing significantly from harmonic form.

Information about the stability of periodic solutions has been obtained using the numerical bifurcation package outlined above. The parameter b_1 is left free and its critical value for fixed b_2 is located by the bifurcation program. For inverse tangent feedback, the leading coefficient β_2 in the asymptotic expansion of the Floquet exponent is found to be negative, indicating stability of the bifurcated periodic solutions. Similar calculations for linear feedback are somewhat ambiguous: calculated values of β_2 are positive, but the estimated error in the β_2 calculation, while smaller in absolute value than the β_2 value, is of similar order of magnitude. Instability of Hopf bifurcations obtained with linear feedback is suggested by these results but not clearly demonstrated. Simulations for linear feedback parameter very near the Hopf bifurcation locus did not produce any stable limit cycles, a result consistent with the bifurcation package indication.

Numerical simulations have been undertaken to explore the parametric dependence of closed-loop periodic solutions when an inverse tangent feedback of the form of Eqn. (36) is applied. Fig. 5 summarizes some of the results obtained for $b_1 = -10$ and for three different values of b_2 for Model I. For $b_2 = 29$ a small perturbation from the reference steady-state leads to one of the two other steady states (which are both stable) depending on the direction of perturbation. For $b_2 = 30$ relaxation-type oscillations are observed. According to the Model I decrement diagram for the added steady states (Fig. 4A), these are still stable for $b_1 = -10$, $b_2 = 30$. Thus, depending on the initial state, the closed-loop reactor state can oscillate as shown in Fig. 5 or can approach asymptotically one of the additional steady states. Such behavior is illustrated in the projections of phase space dynamics onto the $\bar{x} - \bar{y}$ plane shown in Fig. 6.

The added steady states become unstable for $b_2 = 33$, leaving a single limit cycle as the only evident stable structure in phase space (see Fig. 6). For $b_2 = 100$, the three steady states have collapsed into the reference steady state, and oscillations are of higher frequency and smaller amplitude. The temporal profiles of the oscillations are harmonic in form. Oscillations persist even at $b_2 = 1000$.

Numerical simulations of Model II give quite different results. Considering again b_1 fixed at -10, perturbation from the reference steady-state leads to one of the two other steady-states for $b_2 = 33$. At $b_2 = 34$ strange oscillations appear (Fig. 7). This behavior can possibly be attributed to the nearby F_1 bifurcation point for these feedback parameter values (see Fig. 3). As larger values of b_2 are considered, relaxation-type oscillation is evident at $b_2 = 45$. Harmonic oscillations are observed at $b_2 = 75$, while oscillations disappear at $b_2 = 100$ as the reference steady state becomes stable (Fig. 8). This qualitative feature is markedly different from the Model I behavior for increasing b_2.

It should be noted that, for this particular example of N_2O decomposition, discrimination between the two models is possible by steady-state experiments with differing feed concentrations of N_2. This example was used here because of its simplicity to illustrate the properties and potential of the general concept of feedback-induced bifurcation as a tool for dynamic process modeling.

DISCUSSION

This work shows that introduction of feedback can cause otherwise tame catalytic reaction systems to exhibit steady-state multiplicity and stable limit cycles. The form and the occurrence of these phenomena as a function of feedback parameters may be used to verify an assumed model or to discriminate between rival models, even in the case where steady-state and "transient response" data are in close agreement for some of the possible models.

The decrement diagram is extremely useful in visualizing and summarizing the effects of changes in feedback (and also reactor operating and kinetic)

parameters on bifurcations to periodic solutions. The regions in the parameter space where Hopf bifurcation is expected are easily located and insight is gained into the evolution of Hopf-bifurcated solutions with parameter changes. Also, higher order bifurcations of the F type are predicted, and the nonharmonic types of oscillations sometimes observed can be qualitatively explained in view of these higher-order bifurcation effects.

Once the form of the model has been selected, the feedback approach may be successfully used for kinetic parameter estimation. The frequency of a Hopf-bifurcated limit cycle may be found experimentally as a function of the system and feedback parameters. While this limit cycle may have infinitesimal amplitude in the neighborhood of the bifurcation point, the frequency of this cycle will be evident in finite amplitude fluctuations following a pulse disturbance of the closed-loop reactor system. In a laboratory experiment the exact point of bifurcation may of course not be found, but the frequency of the periodic solutions is quite insensitive to small perturbations from the bifurcation point as is clear by the asymptotic expansion of the period of oscillations (Eqn. (5)).

Then, assuming the form of the model is known, the characteristic equation of the Jacobian at the steady state may be expressed in terms of system and feedback parameters. At the point of Hopf bifurcation it is known that the characteristic equation is satisfied by $\lambda = \pm i\omega$, where ω is the measured frequency of the period solutions. Thus, for each bifurcation point, two algebraic equations are obtained (one for the real part of the equation and one for the imaginary). These algebraic equations may then be used in conjunction with steady-state equations to estimate values of kinetic parameters using a least-squares procedure.

Finally, it should be noted that in the above discussion and analysis, measurement, computation and actuation time lags have been assumed negligible. These lags may be significant in some cases, requiring modification in the mathematical description and characterization of the closed-loop system.

NOMENCLATURE

A	linear differential operator
b_1, b_2	feedback parameters
c_{So}	maximum concentration for adsorbed oxygen atoms for Model I (mole/cm^3)
c_{So}'	maximum concentration for adsorbed oxygen atoms for Model II (mole/cm^3)
$c_{N_2O,f}^{0}$	reference feed concentration = 10^{-7} mole/cm^3
c	gas species concentration vector (mole/cm^3)
c_S	surface species concentration vector (mole/cm^3)
c_f	feed concentration vector (mole/cm^3)
E^p	Euclidean p-space
$\tilde{f}_1, \tilde{f}_2$	functions defined in Eqns. (28) and (29)
$\tilde{f}_1', \tilde{f}_2'$	functions defined in Eqns. (37) and (38)
F	function defined in Eqn. (2)
$\hat{F}$	function defined in Eqn. (13)
G	function defined in Eqns. (7-9)
h	increment defined in Eqn. (11)
$D_1, D_2, F_1, F_2, F_3, G_1, G_2, G_3, G_4, G_5$	strata in parameter space
k_i, k_i'	rate constants
M	parameter space
$P_\varepsilon(t)$	periodic solution
q	variable in Eqns. (7-9)
r_1, r_2, r_1', r_2'	reaction rates defined in Eqns. (18,19,22,23)
r_f, r_g	rates of formation (mole/cm^3·sec)
S	catalytic site

$T^H(\varepsilon)$	period of periodic solutions (Eqn. (5))
x	system state vector (Eqn. (1))
x_s	stationary point of vector x
$\tilde{u},\tilde{x},\tilde{y},\tilde{z},\tilde{\omega},\tilde{t},$	dimensionless variables defined in Eqn. (20.6)
$\tilde{u}_s,\tilde{x}_s,\tilde{y}_s,\tilde{z}_s,\tilde{\omega}_s$	reference steady-state values ($\tilde{u}_s = 1$)
$\bar{t}_R$	reactor mean residence time (sec)

GREEK SYMBOLS

α	real part of eigenvalue (Eqn. (3.1))
$\tilde{\alpha},\tilde{\varepsilon},\gamma,\delta$	dimensionless variables of Model I defined in text
α	$c_{So}'/c^0_{N_2O,f}$
β	$k_1' c_{N_2O,f} \bar{t}_R$
γ	$k_2' c_{N_2O,f} \bar{t}_R$
δ	$k_{-2}' c^2_{N_2O,f} \bar{t}_R$
$\beta^H(\varepsilon)$	Floquet exponent (Eqn. (6))
$\varepsilon,\varepsilon^H$	defined in Eqn. (4)
η	bifurcation parameter (Eqns. (7-9))
θ	partial surface coverage $(0 \leq \theta \leq 1)$
$\lambda,\bar{\lambda}$	eigenvalues
μ	parameter vector
$\mu^H(\varepsilon)$	function defined in Eqn. (4)
ν	bifurcation parameter in Eqn. (1)
ν_c	critical value of bifurcation parameter
ω	imaginary part of eigenvalue (Eqn. (3.1))
ω_0	defined in Eqn. (3.1)

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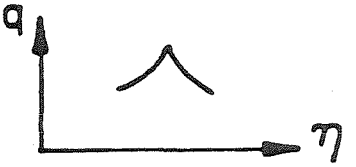
Table 1. Steady-state bifurcations [32]

Defining Conditions at (q_0, η_0)	Bifurcation Diagram
(1) $G = 0$, $G_\eta \neq 0$	
(2) $G = G_q = 0$, $G_{qq} \cdot G_\eta \neq 0$	
(3) $G = G_q = G_\eta = 0$, $G_{qq} \cdot \det d^2G^{\dagger} \neq 0$ index $d^2G = 1^{\neq}$	
(4) $G = G_q = G_\eta = 0$, $G_{qq} \det \cdot d^2G \neq 0$ index $d^2G \neq 1$	
(5) $G = G_q = G_\eta = \det(d^2G) = 0$ $G_{qq} \cdot (d^3G)(v,v,v) \neq 0^{*}$	
(6) $G = G_q = G_{qq} = 0$ $G_{qqq} \cdot G_\eta \neq 0$	
(7) $G = G_q = G_{qq} = G_\eta = 0$ $G_{qqq} \cdot G_{\eta q} \neq 0$	
(8) $G = G_q = G_{qq} = G_\eta = G_{\eta q} = 0$ $G_{qqq} \cdot G_{\eta\eta} \neq 0$	

† d^2G denotes the Hessian of G.

* See condition (iii) (Eqn. 9).

≠ Index $d^2G = 1$ means $\det(d^2G)$ changes sign as bifurcation point is crossed

Table 2. Steady-state values as a function of feed concentration for two different kinetic models of N_2O decomposition

	MODEL I		MODEL II	
$\tilde{u}$	$\tilde{x}$	$\tilde{\omega}$	$\tilde{x}$	$\tilde{\omega}$
0.1	0.084229	8.14987	0.084519	7.97272
0.2	0.168826	8.03723	0.169185	7.97282
0.3	0.253650	7.95355	0.253992	7.88432
0.4	0.338653	7.88476	0.338934	7.84211
0.5	0.423805	7.82544	0.424006	7.80115
0.6	0.509088	7.77279	0.509202	7.76135
0.7	0.594488	7.72519	0.594517	7.72265
0.8	0.679993	7.68156	0.679948	7.68499
0.9	0.765596	7.64117	0.765489	7.64831
1.0	0.851290	7.60348	0.851138	7.61258
1.1	0.937068	7.56806	0.936890	7.57740
1.2	1.022920	7.53463	1.022740	7.54375
1.3	1.108860	7.50292	1.108690	7.51057
1.4	1.194860	7.47273	1.194730	7.47817
1.5	1.280930	7.44390	1.280870	7.44651
1.6	1.367070	7.41628	1.367709	7.41555
1.7	1.453270	7.38977	1.453388	7.38528
1.8	1.539520	7.36425	1.539776	7.35565

CAPTIONS TO FIGURES

Figure 1. "Transient response" comparison for both models of N_2O decomposition in a catalytic CSTR following a step change in feed N_2O concentration.

Figure 2. Decrement diagram for Model I with inverse tangent feedback. The reference steady-state is unstable for the closed-loop system for feedback gains in the region left of the dashed line. The heavy solid line divides the parameter plane into regions with one and three steady states. The D_2 region is stippled while the D_1 region is clear.

Figure 3. Decrement diagram for Model II with inverse tangent feedback (notation as in Fig. 2).

Figure 4. Decrement diagrams for the added steady states for Models I and II with inverse tangent feedback. These steady states are unstable for feedback gains above the dotted line and below the steady-state multiplicity line.

Figure 5. Periodic solutions for closed-loop operation with Model I and arctan feedback for $(b_1,b_2) = (10,30)$, ——— ; $(-10,100)$, - - - - ; $(-10,1000)$, • • • • .

Figure 6. Projection of concentration trajectories onto the $\tilde{x}-\tilde{y}$ plane for Model I with inverse tangent feedback for different gain parameters (A: $b_1 = -10$, $b_2 = 30$; B: $b_1 = -10$, $b_2 = 33$).

Figure 7. Periodic solution of Model II in closed-loop operation with arctan feedback; $(b_1, b_2) = (-10, 34)$.

Figure 8. Changes in the closed-loop response of Model II with arctan feedback and $(b_1, b_2) = (-10, 45)$, ——— ; $(-10, 75)$, - - - - .

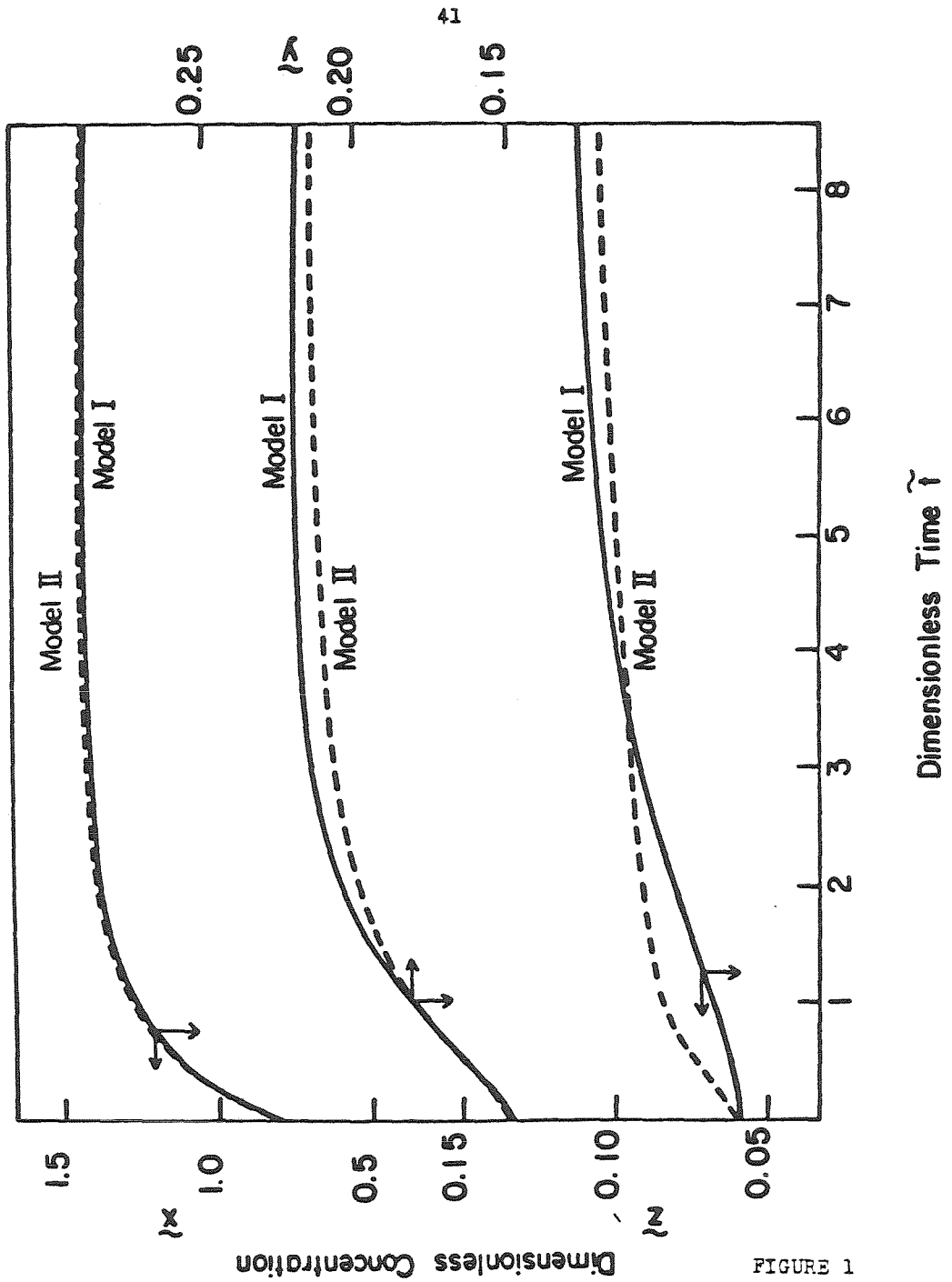

Dimensionless Concentration
Dimensionless Time $\tilde{t}$
x_1
y_1
z_1
Model I
Model II
Model I
Model II
Model I
Model II
1.5
1.0
0.5
0.15
0.10
0.05
0.25
0.20
0.15
1
2
3
4
5
6
7
8

FIGURE 1

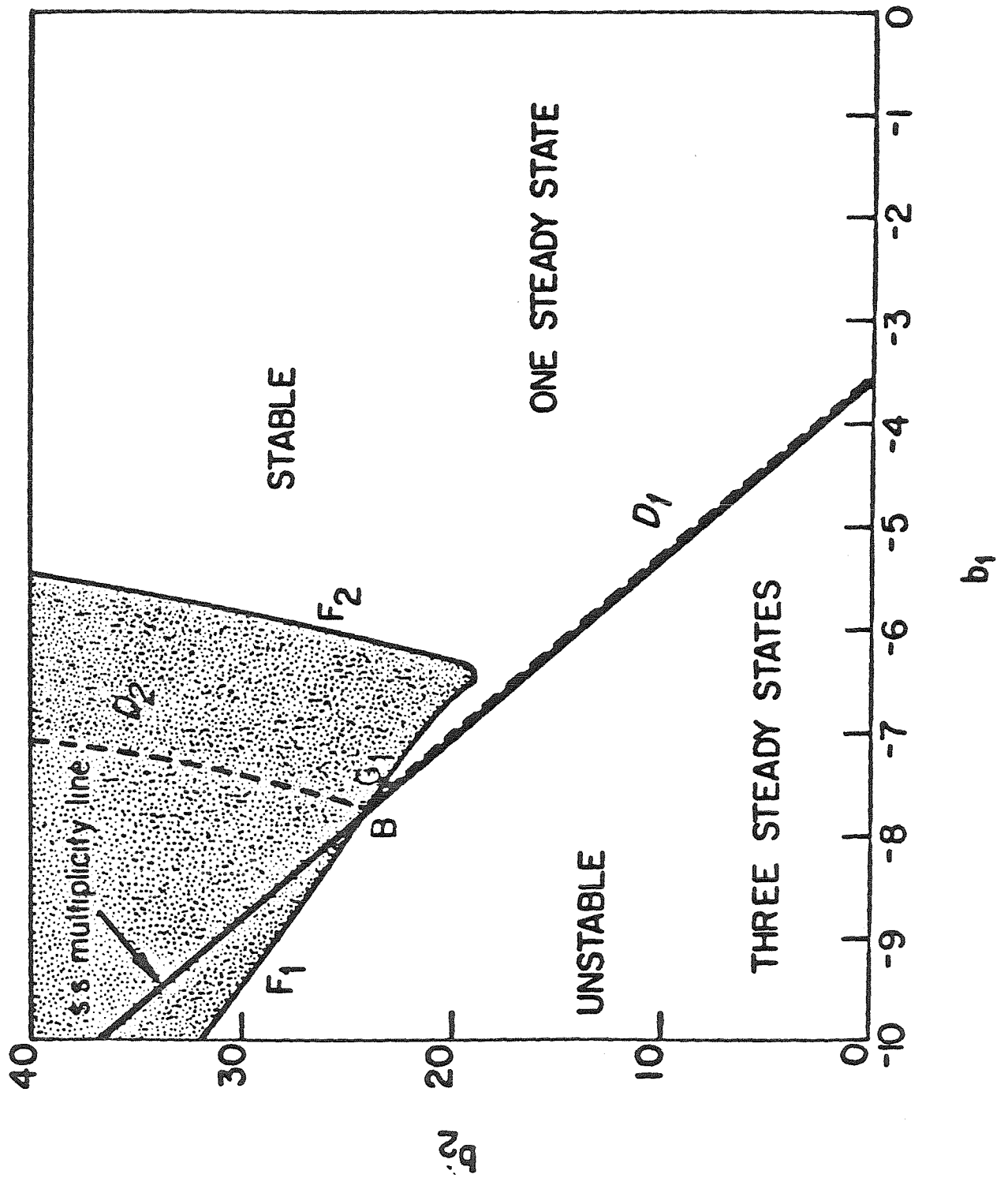

STABLE
ONE STEADY STATE
UNSTABLE
THREE STEADY STATES
s.s multiplicity line
F_1
F_2
G_1
G_2
B
D_1
40
30
20
10
0
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
a_2
b_1

FIGURE 2

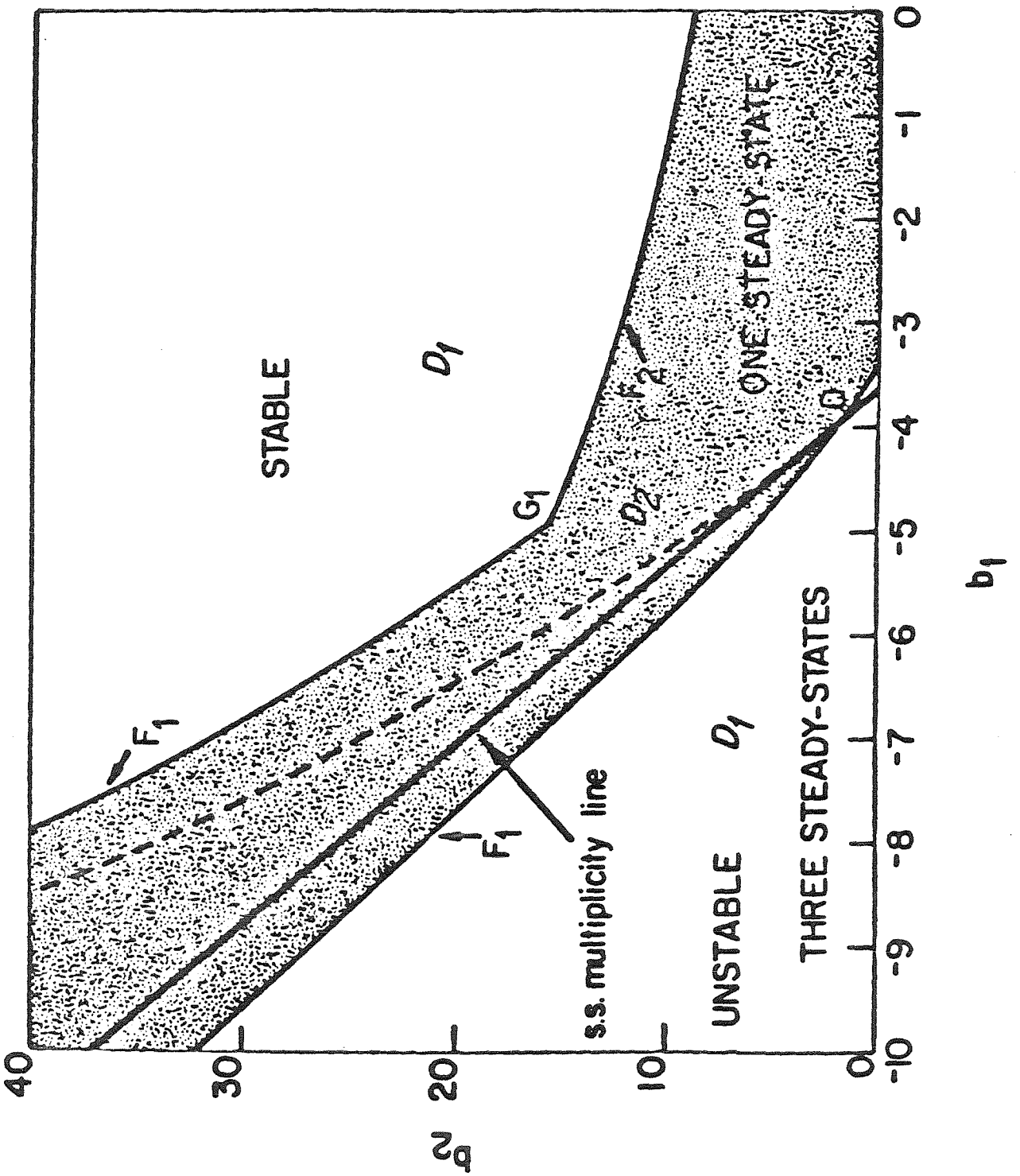

STABLE
D_1
G_1
F_2
D_2
ONE STEADY-STATE
F_1
s.s. multiplicity line
F_1
UNSTABLE
D_1
THREE STEADY-STATES
40
30
20
10
0
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
b_2
b_1

FIGURE 3

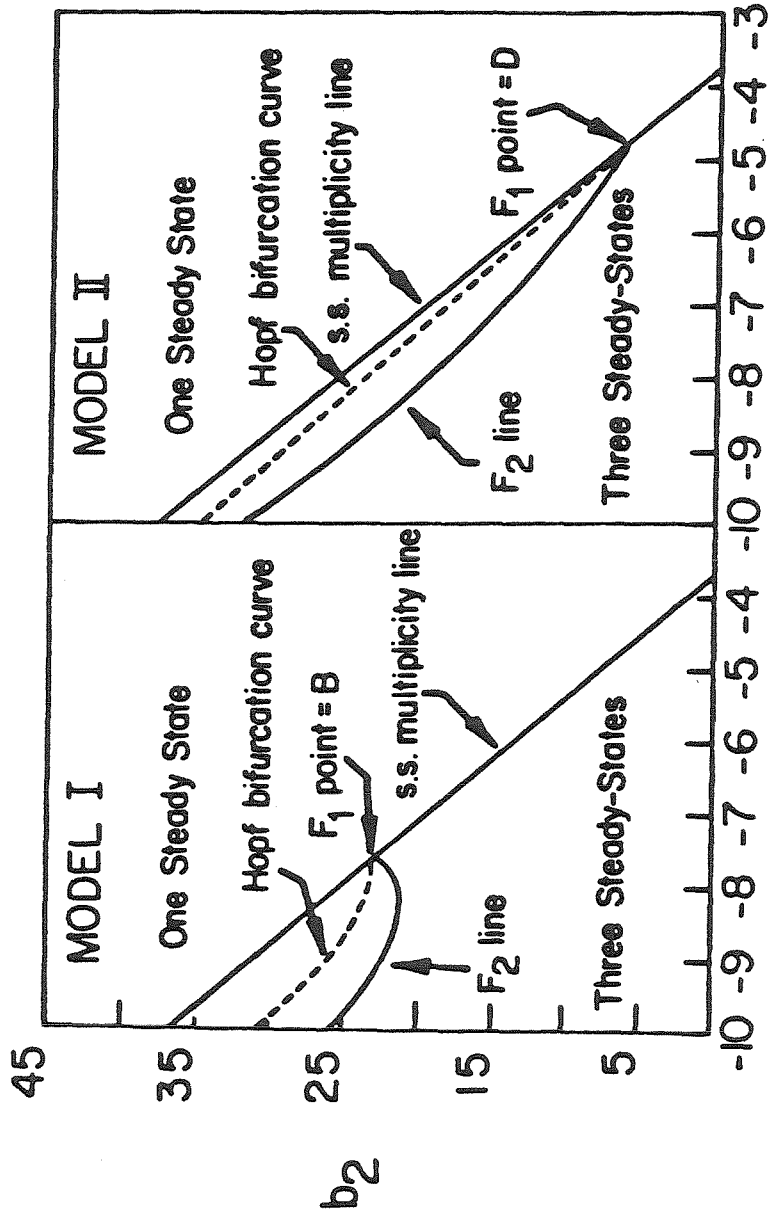

MODEL I
One Steady State
Hopf bifurcation curve
F_1 point = B
s.s. multiplicity line
F_2 line
Three Steady-States
MODEL II
One Steady State
Hopf bifurcation curve
s.s. multiplicity line
F_1 point = D
F_2 line
Three Steady-States
45
35
25
15
5
b_2
-10 -9 -8 -7 -6 -5 -4 -10 -9 -8 -7 -6 -5 -4 -3
b_1

FIGURE 4

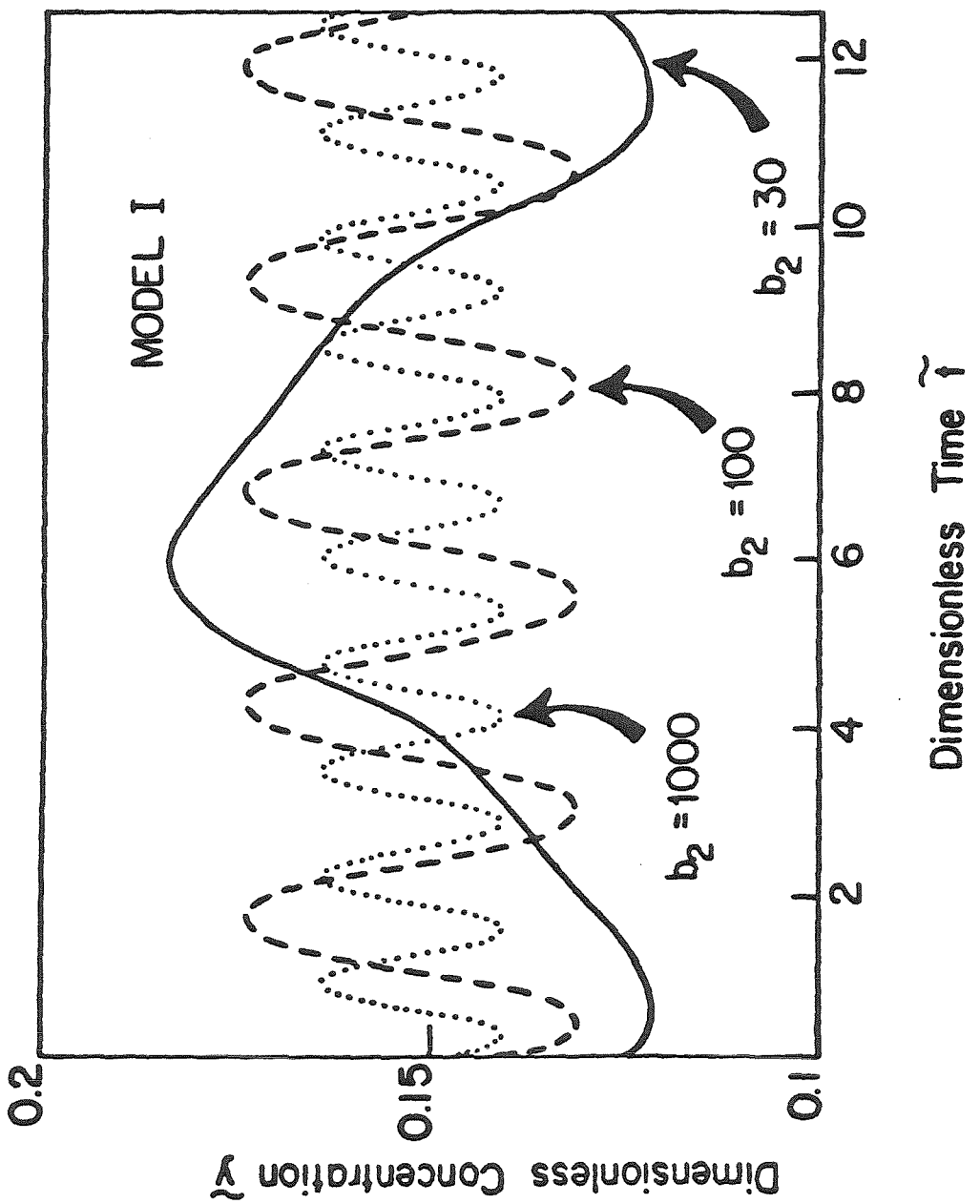

MODEL I
$b_2 = 1000$
$b_2 = 100$
$b_2 = 30$
0.2
0.15
0.1
2
4
6
8
10
12
Dimensionless Concentration $\tilde{y}$
Dimensionless Time $\tilde{t}$

FIGURE 5

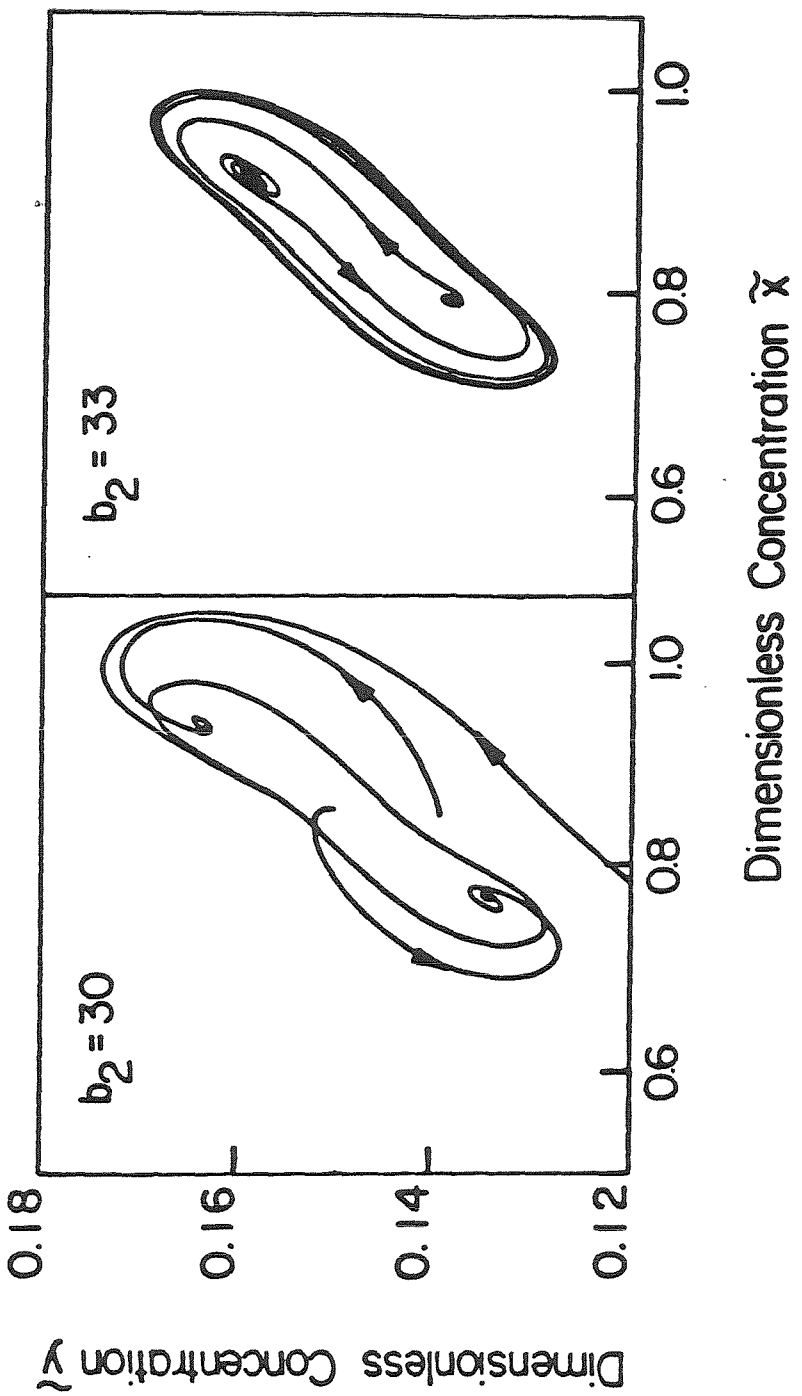

$b_2 = 30$
$b_2 = 33$
0.18
0.16
0.14
0.12
0.6
0.8
1.0
0.6
0.8
1.0
Dimensionless Concentration $\tilde{y}$
Dimensionless Concentration $\tilde{x}$

FIGURE 6

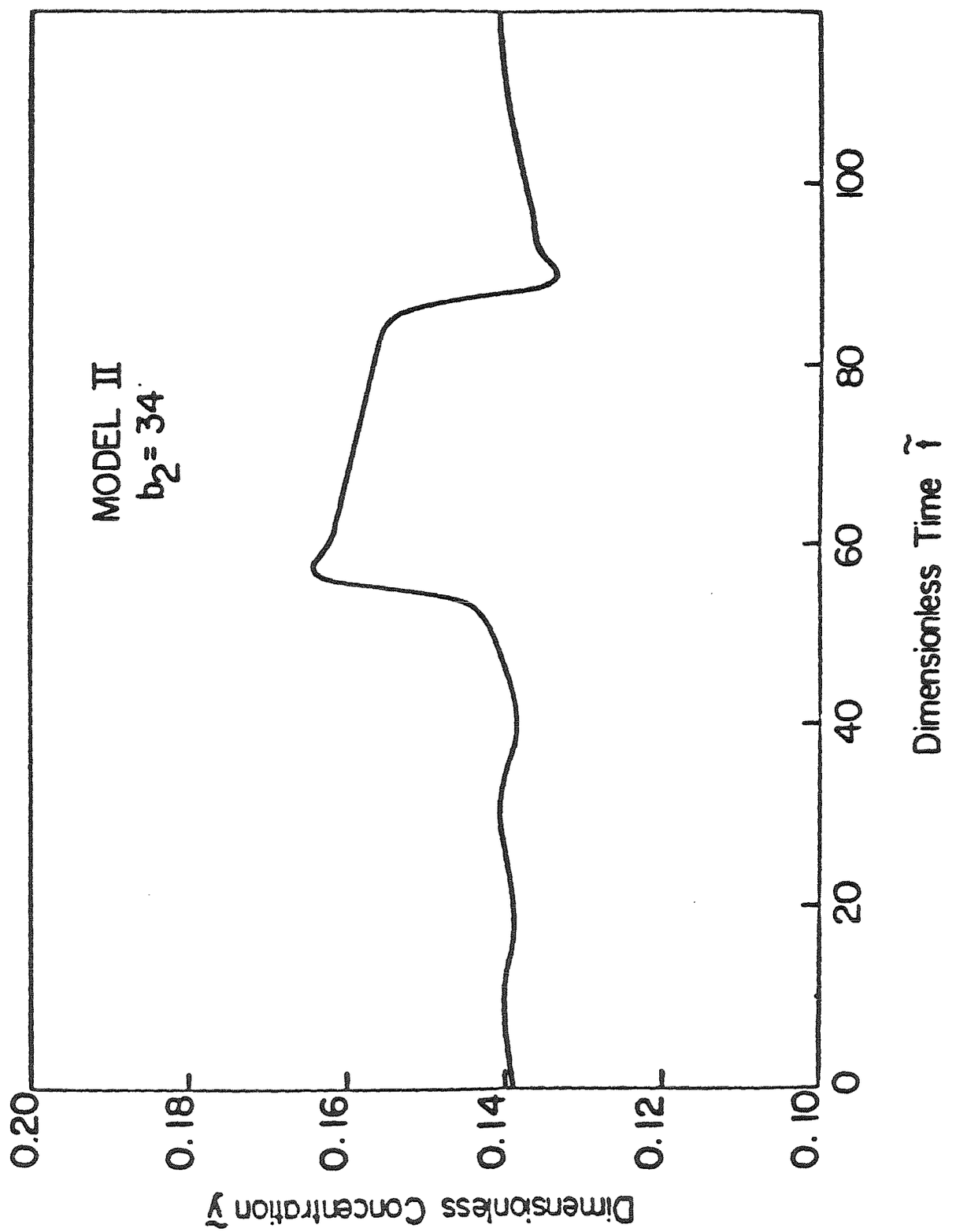

MODEL II
$b_2 = 34$
Dimensionless Concentration $\tilde{y}$
0.20
0.18
0.16
0.14
0.12
0.10
0
20
40
60
80
100
Dimensionless Time $\tilde{t}$

FIGURE 7

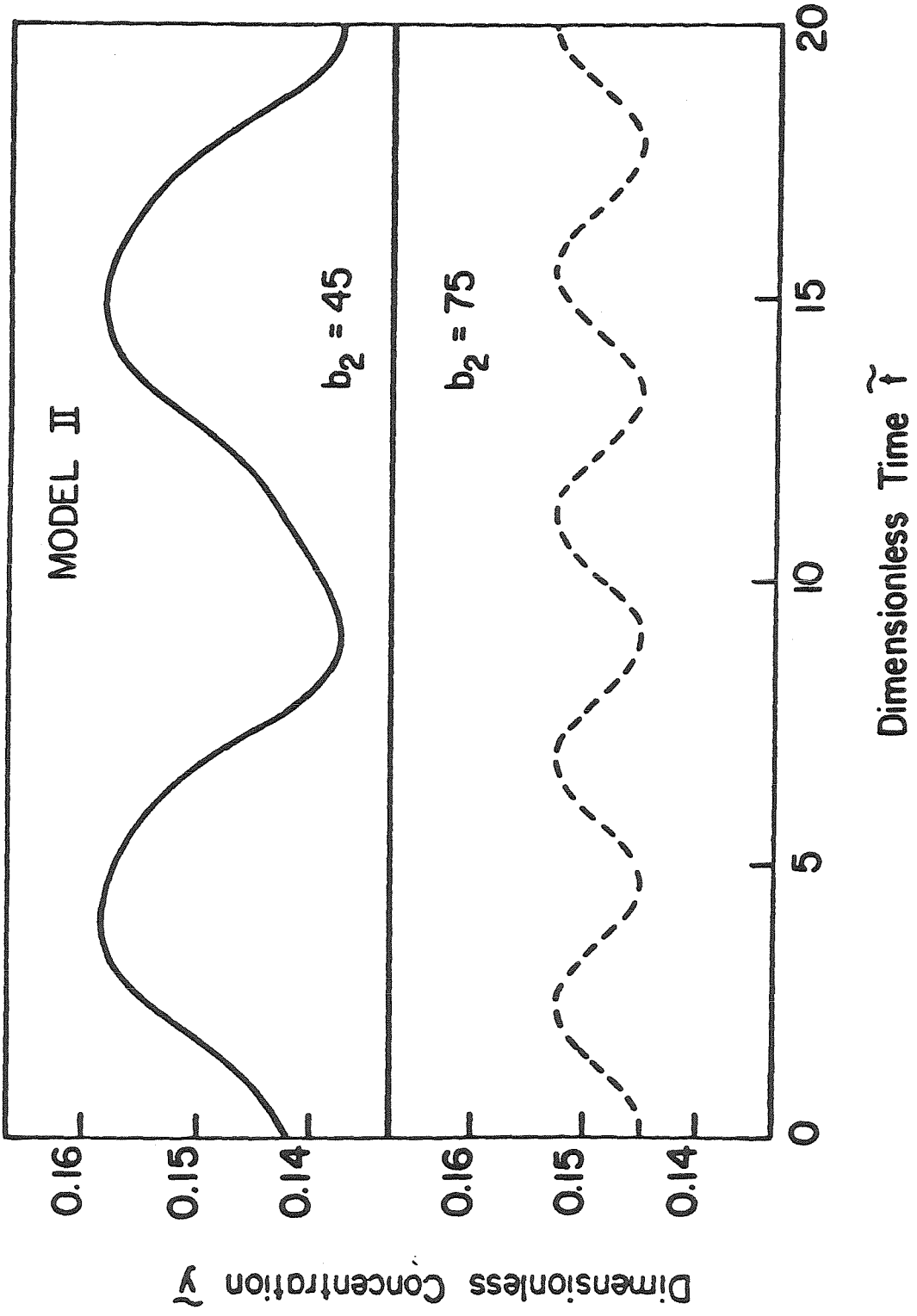

MODEL II
$b_2 = 45$
$b_2 = 75$
0.16
0.15
0.14
0
5
10
15
20
Dimensionless Time $\tilde{t}$
Dimensionless Concentration $\tilde{y}$

FIGURE 8

CHAPTER 3 : STEADY-STATE MULTIPLICITY AND BIFURCATION ANALYSIS VIA THE NEWTON POLYHEDRON APPROACH

INTRODUCTION

Steady-state multiplicity has been observed and theoretically predicted on many occasions in chemical reactor theory and is a property of paramount importance when studying the operating characteristics of any chemical reaction system. This phenomenon, first popularized by Van Heerden in 1953 [1], has since drawn the attention of many workers [2-11]. Heinemann *et al.* [12] applied the Keller method [13] for finding solution branches computationally in the parameter region of interest for a combustion problem. Balakotaiah and Luss [14] applied Golubitsky's bifurcation theory [15] to identify parameter values at steady-state bifurcation and the local solution surface near the bifurcation point.

In almost all problems considered previously it has been possible to reduce the model steady-state equations to a single scalar nonlinear equation in one unknown. This reduction is not possible for many other systems of interest. Using Keller's linear algebraic approach for multiple nonlinear equations, one requires that a necessary condition for bifurcation be satisfied: the determinant of the Jacobian must vanish. Supplementary bifurcation conditions involving the derivatives of the algebraic equations with respect to the bifurcation parameter must also be satisfied to ensure bifurcation. In this approach choosing the bifurcation parameter is an essential and critical step. Further, one must compute the derivatives appearing in the bifurcation conditions [13].

The objective of this work is to introduce and illustrate an extremely powerful mathematical tool, the Newton polyhedron method, for determining bifurcation points of steady-state solutions. This method can be applied when the steady-state equations cannot be reduced to a single equation or where pro-

hibitive algebraic effort and complexity would arise in such a reduction. One major advantage of the Newton polyhedron method is simultaneous consideration of all system parameters in the algebraic conditions that must be satisfied at bifurcation. One does not need to choose a single, particular bifurcation parameter. Furthermore, in the case where the model steady-state equations are of polynomial form, no evaluation of partial derivatives is required.

The method is applied here to two chemical reaction engineering problems. The first is isothermal reaction between two adsorbed species in a catalytic CSTR, a system for which the steady-state material balances have polynomial form. The method is used to examine the steady-state multiplicity produced when feedback manipulation of input concentration is added to the reactor, a strategy suggested previously for catalytic reaction model discrimination [16]. The second problem considers two and three parallel reactions of arbitrary order taking place in a nonisothermal CSTR. Here reduction to one steady-state equation is in general impossible. Criteria are obtained for absence of bifurcation to multiple steady-states from a basic solution branch, and, for a specific problem of one second order and one third order reaction, the point in parameter space at which steady-state bifurcation occurs is found.

THEORETICAL BACKGROUND

Consider the system of k-algebraic equations in k unknowns $\xi_1,\ldots,\xi_k$:

$$\begin{aligned} f_1(\xi_1,\ldots,\xi_k) &= 0 \\ f_2(\xi_1,\ldots,\xi_k) &= 0 \\ f_k(\xi_1,\ldots,\xi_k) &= 0 \end{aligned} \qquad (1)$$

Suppose that $\underline{\xi}_0 = (\xi_{10}, \ldots, \xi_{k0})$ is a solution of system (1). (Only real solutions are considered throughout this work. The *Milnor number* $\mu_f(\underline{\xi}_0)$ is defined as the multiplicity of the solution $\underline{\xi}_0$. By multiplicity here is understood the number of solutions of (1) when one or more parameters of system (1) are slightly perturbed from their original values for which $\underline{\xi}_0$ is a solution. Usually perturbation in one direction produces $\mu_f(\underline{\xi}_0)$ solutions, whereas perturbation in the opposite direction retains the same solution configuration.

The definition of multiplicity used here, which refers to bifurcation and *local* appearance of additional steady-state solutions, should not be confused with the use of the term steady-state multiplicity elsewhere in chemical engineering. Often, in other works on steady-state multiplicity, one is concerned with multiple roots of Eqn. (1) which may be widely separated. To illustrate the difference between the multiplicity *of a solution* and the multiplicity of *the solutions* to a system of equations, consider the single equation $w^3 - bw = 0$. For $b = 0$, the solution $w = 0$ has multiplicity three ($\mu_f(0) = 3$) perturbing the parameter b to some positive value, three solutions to the equation exist. Notice, however, that for $b > 0$, each of the three solutions has multiplicity unity. Near each, there is only a single solution branch. Sufficiently small perturbations in b about any positive value do not alter the number of solutions.

As will be stated precisely in the main theorem below, the multiplicity of the solution ξ_0 is often equal to and is never less than an integer called the *Newton number* ν. The Newton number depends only on the functional form of the system of equations and can be evaluated directly after identification and characterization of the dominant features of the equations. The concepts required for calculation of the Newton number are summarized next.

Suppose for the present that each of the functions f_i in Eqn. (1) is a polynomial (generalization to other smooth nonlinear functions follows below). Defining deviation variables $x_i = \xi_i - \xi_{i0}$, each function f_i may be written as follows:

$$f_i(x_1,\ldots,x_k) = \sum_{\underline{n}\in Z^k} \alpha_{ni}\underline{x}^{\underline{n}} \tag{2}$$

where $\underline{x}^{\underline{n}} \equiv x_1^{n_1}\ldots x_k^{n_k}$ is a monomial in variables $x_1,\ldots,x_k$. Thus, each $\underline{n} = (n_1,\ldots,n_k)\in Z^k$. Consider for example the system:

$$\begin{aligned} f_1'(x_1,x_2) &= 2\delta x_1 + x_1^2 - 3x_2^3 = 0 \\ f_2'(x_1,x_2) &= x_1 - x_2^3 + 2x_2^4 + x_1^5 = 0 \quad . \end{aligned} \tag{3}$$

Clearly, (0,0) is a solution of system (3). System (3) can be written in the form of Eqn. (2):

$$\begin{aligned} f_1' &= \alpha_{n_1}\underline{x}^{\underline{n}_1} + \alpha_{n_2}\underline{x}^{\underline{n}_2} + \alpha_{n_3}\underline{x}^{\underline{n}_3} \\ f_2' &= \beta_{m_1}\underline{x}^{\underline{m}_1} + \beta_{m_2}\underline{x}^{\underline{m}_2} + \beta_{m_3}\underline{x}^{\underline{m}_3} + \beta_{m_4}\underline{x}^{\underline{m}_4} \end{aligned} \tag{4}$$

where

$$\underline{n}_1 = (1,0) \quad , \quad \underline{n}_2 = (2,0) \quad , \quad \underline{n}_3 = (0,3)$$

$$\underline{m}_1 = (1,0) \quad , \quad \underline{m}_2 = (0,3) \quad , \quad \underline{m}_3 = (0,4) \quad , \quad \underline{m}_4 = (5,0)$$

and

$$\alpha_{n_1} = 2\delta \; , \quad \alpha_{n_2} = 1 \quad , \quad \alpha_{n_3} = -3$$

$$\beta_{m_1} = 1 \quad , \quad \beta_{m_2} = -1 \quad , \quad \beta_{m_3} = 2 \quad , \quad \beta_{m_4} = 1 \quad .$$

The *supports of* f_i are defined as the numbers $\underline{n} \epsilon Z^k$ such that $\alpha_{n_i} \neq 0$. The set of all supports $\text{supp} f_i$ is consequently given by

$$\text{supp} f_i = \left\{ \underline{n} \epsilon Z^k : \alpha_{n_i} \neq 0 \right\} \quad . \tag{5}$$

The *Newtonian principal part* of the polynomial f_i is defined to be the following polynomial:

$$\tilde{f}_{i0} = \sum_{\underline{n} \epsilon \bar{\Gamma}(f_i)} \alpha_{n_i} \underline{x}^{\underline{n}} \quad . \tag{6}$$

For the polynomials of Eqn. (3), the Newtonian principal parts are:

$$\begin{aligned} \tilde{f}'_{10} &= 2x_1 - 3x_2^3 \\ \tilde{f}'_{20} &= x_1 - x_2^3 \quad . \end{aligned} \tag{7}$$

For the system of Eqn. (3), the supports are

$$\text{suppf}_1' = \{(1,0)\ ,\ (2,0)\ ,\ (0,3)\}$$

$$\text{suppf}_2' = \{(1,0)\ ,\ (0,3)\ ,\ (0,4)\ ,\ (5,0)\}\ .$$

The *Newton diagram* of f_i is simply a graph in k-space of the members of suppf_i. The Newton diagrams for functions f_1' and f_2' of the example are illustrated by the dots in parts (A) and (B), respectively, of Figure 1. The polynomial $f_i = \sum_{\underline{n}\in Z^k} a_{n_i} \underline{x}^{\underline{n}}$ is called *proper* [17] if, for all j from 1 to k, a monomial $x_j^{n_j}$ $(n_j \geq 1)$ appears in f_i with a nonzero coefficient. Both polynomials in the example of Eqns. (3) are proper. The corresponding Newton diagram is proper if all positive coordinate axes contain at least one point of the diagram.

Let

$$\tilde{\Gamma}_-(f_i) = \{\text{convex envelope with respect to the origin* of the set } \text{suppf}_i \cap R_+^k\}$$

where R_+^k denotes the nonnegative orthant of R^k. The shaded regions in Figure 1A and 1B illustrate $\tilde{\Gamma}(f_1')$ and $\tilde{\Gamma}(f_2')$, respectively, for the functions in Eqn. (3). The *Newton frontier* is defined as the following polyhedron: defined as the following polyhedron:

$$\tilde{\Gamma}(f_i) = \{\text{the set of all closed faces of the polyhedron } \tilde{\Gamma}_-(f_i)\}\ .$$

Again, Figure 1 shows clearly the Newton frontiers for f_1 and f_2 of Eqn. (2).

---

*Let P be any (k-1) dimensional plane which separates the origin from all elements of the set $S \subset R^k$ and let P^+ denote the closed half-space on the side of P which includes S. The convex envelope of the set S with respect to the origin is the intersection of all such half-spaces P^+.

Let V denote the volume of the subdomain of the nonnegative orthant in R^k lying below the Newton frontier $\tilde{\Gamma}(f_i)$, V_j denote the (k-1)-dimensional volume under the Newton frontier on the jth coordinate hyperplane, $V_{j\ell}$ denote the (k-2)-dimensional volume on the coordinate plane orthogonal to the jth and ℓth basis vector, and so forth. Then the *Newton number* $\nu(\Gamma)$ of Γ is defined as:

$$\nu(\Gamma) = k!V - (k-1)! \sum_{j=1,k} V_j + (k-2)! \sum_{\substack{j=1,k \\ \ell=1,k \\ j<\ell}} V_{j\ell} - \ldots + (-1)^k \quad . \tag{8}$$

Consider for example the polynomial f_1' in Eqn. (3). In this case k=2, and Eqn. (8) becomes:

$$\nu(\Gamma_{f_1'}) = 2!V - 1!(V_1 + V_2) + 1 \quad . \tag{9}$$

Now V is just the area under the Newton frontier and is equal to $V = \frac{1}{2} \times 1 \times 3 = \frac{3}{2}$; $V_1 = 1$ while $V_2 = 3$. Substituting these values in Eqn. (9) gives:

$$\nu(\Gamma_{f_1'}) = 0 \quad . \tag{10}$$

Similarly for f_2'

$$\nu(\Gamma_{f_2'}) = 2!\left(\frac{1}{2} \cdot 1 \cdot 3\right) - 1!(1+3) + 1 = 0 \quad . \tag{11}$$

The Newton number is defined somewhat differently for the *system* of Eqns. (1). For such a k-dimensional system, the mixed Minkowski volume U is defined as [18]:

$$U = (-1)^{k-1} \sum_{i=1,k} V_k(S_i) + (-1)^{k-2} \sum_{\substack{i=1,k \\ q=1,k \\ i<q}} V_k(S_i + S_q) + \ldots + V_k(S_1 + \ldots + S_k) \tag{12}$$

Here $V_k(S_i)$ is the Euclidean volume under the Newton frontier (f_i). To find $S_i + S_q$, one simply multiplies the polynomials f_i and f_q and considers the Newton frontier of the resulting polynomial. Similarly, to find $S_1+\ldots+S_k$, the Newton diagram of the product $f_1 \cdot f_2 \cdot \ldots \cdot f_k$ is considered. Then, the Newton number for the system (1) is $\nu = U$.

Now that the required concepts have been introduced, a central theorem can be stated:

> Theorem [Bernshtein, 18]: The Milnor number $\mu_f(\underline{\xi}_0)$ is greater than or equal to the Newton number $\nu(\Gamma(f))$. The Milnor and Newton numbers are equal apart from a measure zero set of parameter values of the polynomials f_1 through f_k (a degenerate case). In a degenerate case, the Milnor number is greater than the Newton number.

As an example consider the system given by Eqn. (3). Equation (12) in this case is:

$$U = -V_2(S_1) - V_2(S_2) + V_2(S_1 + S_2) \quad . \tag{13}$$

Clearly

$$V_2(S_1) = \frac{1}{2} \cdot 1 \cdot 3 = \frac{3}{2} \quad ,$$

and

$$V_2(S_2) = \frac{1}{2} \cdot 1 \cdot 3 = \frac{3}{2} \quad .$$

Finally to find $S_1 + S_2$ one needs:

$$\begin{aligned} f_1' \cdot f_2' = {} & 2x_1^2 + x_1^3 + 2x_1^6 + x_1^7 + 3x_2^6 - 6x_2^7 \\ & -5x_1x_2^3 + 2x_1^2x_2^4 + 4x_1x_2^4 - x_1^2x_2^3 - 3x_1^5x_2^3 \quad . \end{aligned} \tag{14}$$

The Newton diagram of this polynomial is also presented in Fig. 1, from which

$$V_2(S_1 + S_2) = \frac{1}{2} \cdot 2 \cdot 6 = 6 \quad . \tag{15}$$

Then Eqn. (13) becomes:

$$U' = \nu = -\frac{3}{2} - \frac{3}{2} + 6 = 3 \quad . \tag{16}$$

According to the Bernshtein Theorem, this implies that, unless the system is degenerate, the multiplicity of the zero solution of system (2) is three.

In many problems of interest in chemical engineering, the Newton number is unity. Then, according to the Bernshtein Theorem, steady-state bifurcation is not possible unless a degenerate case occurs. Because of this importance of degenerate situations, useful degeneracy conditions are next presented.

Degeneracy Condition

The Newtonian principle part of a polynomial f_i is nondegenerate if and only if for each closed face Δ of the Newton frontier the Laurent polynomials

$$x_1\left(\frac{\partial f_i}{\partial x_1}\right)_\Delta, \ \ldots \ , \ x_k\left(\frac{\partial f_i}{\partial x_k}\right)_\Delta$$

do not vanish simultaneously. If the dimension of Δ ($\dim(\Delta)$) is s and the number of points of the set suppf_i on Δ is equal to s+1, then the Newtonian principal par nondegenerate on Δ for any nonzero values of the coefficients of f_i [17]. The nondegeneracy condition for the case $\dim(\Delta) = s$ and with s+2 points of the set suppf_i on Δ will be explicitly developed next.

Without loss of generality one can admit that $\dim(\Delta) = s = k - 1$. Then the restriction of f_i on the face of the Newton frontier, denoted $f_{i\Delta}$, can be written as

$$f_{i\Delta} = a_0 \underline{x}^{\underline{m}_0} + \ldots + a_k \underline{x}^{\underline{m}_k} \tag{17}$$

where $\underline{m}_0, \ldots, \underline{m}_k \in Z^k$. There exists a set $(d_0, \ldots, d_k)$ of integer numbers with no common divisor, unique up to a sign, which satisfy the system of k equations in k+1 variables:

$$d_0 \underline{m}_0 + \ldots + d_k \underline{m}_k = 0 \quad . \tag{18}$$

Let $Z_0 = \underline{x}^{\underline{m}_0}, \ldots, Z_k = \underline{x}^{\underline{m}_k}$ and define the Lagrange function

$$L(Z,\lambda) = \alpha_0 Z_0 + \cdots + \alpha_k Z_k + \lambda(1 - Z_0^{d_0} \cdot \ldots \cdot Z_k^{d_k}) \quad . \tag{19}$$

The function $f_{i\Delta}$ is degenerate on Δ if and only if the system

$$\frac{\partial L}{\partial \lambda} = \frac{\partial L}{\partial Z} = 0 \tag{20}$$

has a solution [17].

Writing explicitly the system of Eqns. (20), one obtains

$$\begin{aligned} \alpha_0 Z_0 &= \lambda d_0 \\ &\cdots\cdots\cdots \\ \alpha_k Z_k &= \lambda d_k \\ Z_0^{d_0} \cdot \ldots \cdot Z_k^{d_k} &= 1 \quad . \end{aligned} \tag{21}$$

This system has no solution if at least one of the numbers d_i is zero. However, for nonzero d_i, system (21) has a solution if and only if [17]:

$$\left(\frac{\alpha_0}{d_0}\right)^{d_0} \cdot \ldots \cdot \left(\frac{\alpha_k}{d_k}\right)^{d_k} = 1 \quad . \tag{22}$$

This procedure may be generalized for the case in which there are more than $s+2$ points on the face Δ.

When considering the system of Eqns. (1), one should check for degeneracy not only on each individual Newton frontier of f_i, $i = 1, \ldots, k$ but also on the Newton frontier of $S_i + S_q, \ldots, S_1 + S_2 + \cdots + S_k$. Unless the polynomial coefficients satisfy the degeneracy condition on at least one of these frontiers, the Bernshtein Theorem [18] guarantees that the multiplicity of the solution to the system of equations is equal to the Newton number.

For the example system (3) (see Fig. 1), one can easily see that $k = 2$ and $s = 1$ and that there are only $s + 1 = 2$ supports on the faces of the Newton frontier for f_1' and for f_2'. Consequently, degeneracy is possible only on the frontier face of the $f_1' \cdot f_2'$ Newton diagram. The monomials that can give rise to degeneracy in this case have supports with $\underline{m}_0$, $\underline{m}_1$, and $\underline{m}_2$ given by (2,0), (1,3) and (0,6), respectively. Using these in Eqn. (18) gives $d_0 = 1$, $d_1 = -2$, and $d_2 = 1$ so that the degeneracy condition (22) in this case becomes:

$$4\alpha_0\alpha_2 - \alpha_1^2 = 0 \quad . \tag{23}$$

The coefficients of the Newtonian principal part in Eqn. (14) ($\alpha_0 = 2\delta, \alpha_1 = -2\delta - 3$ $\alpha_2 = 3$) do not satisfy Eqn. (23) unless $\delta = 3/2$. Consequently, unless $\delta = 3/2$, the system is nondegenerate, and the multiplicity is indeed three (equal to the Newton number (Eqn. 16)). For $\delta = 3/2$, the multiplicity exceeds three.

Although the theory has been presented for f_1, ..., and f_k polynomial functions, all the results apply for any function that can be represented near the solution ξ_{10}, ..., ξ_{k0} by a Taylor expansion (or even a Laurent expansion) [20]. This extension is justified by the "filtering out" of all supports above the Newton frontier: these do not influence the multiplicity of the solution [21]. Thus suppose the number of steady-state equations is reduced to two.

$$\left.\begin{aligned} g_1(x_1,x_2) &= 0 \\ g_2(x_1,x_2) &= 0 \end{aligned}\right\} \tag{24}$$

where g_1 and g_2 are not polynomials. Taylor expanding one obtains:

$$\begin{aligned} \tilde{g}_1(x_1,x_2) &= \left.\frac{\partial g_1}{\partial x_1}\right|_0 \cdot x_1 + \left.\frac{\partial g_1}{\partial x_2}\right|_0 \cdot x_2 + O(x^2) = 0 \\ \tilde{g}_2(x_1,x_2) &= \left.\frac{\partial g_2}{\partial x_1}\right|_0 \cdot x_1 + \left.\frac{\partial g_2}{\partial x_2}\right|_0 \cdot x_2 + O(x^2) = 0 \quad . \end{aligned} \tag{25}$$

If none of the first partial derivatives vanishes, there is a possibility of degeneracy. This degeneracy occurs in the Newton polygon of $\tilde{g}_1 \cdot \tilde{g}_2$ when

$$\left(\frac{\partial g_1}{\partial x_1}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_2}\bigg|_0 + \frac{\partial g_1}{\partial x_2}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_1}\bigg|_0\right)^2$$

$$- 4\left(\frac{\partial g_1}{\partial x_1}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_1}\bigg|_0 \cdot \frac{\partial g_1}{\partial x_2}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_2}\bigg|_0\right) \tag{26}$$

$$= \left(\frac{\partial g_1}{\partial x_1}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_2}\bigg|_0 - \frac{\partial g_1}{\partial x_2}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_1}\bigg|_0\right)^2 = 0$$

or

$$\frac{\partial g_1}{\partial x_1}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_2}\bigg|_0 - \frac{\partial g_1}{\partial x_2}\bigg|_0 \cdot \frac{\partial g_2}{\partial x_1}\bigg|_0 = 0 \quad , \tag{27}$$

which indicates that the determinant of the Jacobian is zero, a necessary condition for bifurcation according to [13].

Two-Dimensional Case

The Newton polyhedron approach becomes particularly simple in the case of only two algebraic equations. For this reason this situation deserves special consideration. Consider the system:

$$\begin{aligned} f_1(x_1, x_2) &= 0 \\ f_2(x_1, x_2) &= 0 \end{aligned} \tag{28}$$

It is assumed that transfer of origin has already been made so that the system has the solution $x_1 = x_2 = 0$. In this case $k = 2$. Writing each f_i in the form of Eqn. (2) gives:

$$f_1 = \sum_{\underline{n}\in Z^2} a_{n_1} \underline{x}^{\underline{n}}$$
$$f_2 = \sum_{\underline{n}\in Z^2} a_{n_2} \underline{x}^{\underline{n}} \qquad (29)$$

Construction of the Newton frontier will first be explained for a proper Newton diagram (monomials x_1^{α} and x_2^{β} appear in the polynomial). Simply place a ruler along the x_2-axis. Then rotate the ruler counterclockwise, centered at the support corresponding to the lowest power monomial of the form x_2^{β}, until another support is hit. Continue the rotation in the same sense with the new support as a center this time. Repeat this change of center and rotation step until the ruler hits a support on the x_1-axis. S is the shaded region beneath the Newton frontier. Application of formula (8) yields:

$$\nu(\Gamma_1) = 2S_1 - \alpha_1 - \beta_1 + 1$$
$$\nu(\Gamma_2) = 2S_2 - \alpha_2 - \beta_2 + 1 \qquad (30)$$

where α_1, α_2 and β_1, β_2 are the integer powers of the supports on the axes. The Newton number for the system (28) is given by (from Eqn. (12)):

$$\nu = U = S(f_1 \cdot f_2) - S(f_1) - S(f_2) \quad . \qquad (31)$$

Thus all that is needed is the area under the Newton frontier of f_1, f_2 and $f_1 \cdot f_2$. Arnold [19] has proven that the Newton number in the two-dimensional case may be calculated immediately using the formula:

$$\nu = \min(\alpha_1\beta_2, \alpha_2\beta_1) \qquad (32)$$

Thus, for system (3),

$$\nu = \min(3\cdot 1, 1\cdot 3) = 3 \quad .$$

Before any conclusion about the multiplicity of the solution is reached, the system must be examined for degeneracy. Each face of each Newton diagram must be checked for degeneracy. Consider any face Δ of the Newton diagram in Fig. 2. The dimension of the frontier is clearly k-1 = 1. Thus if on a face

of the Newton frontier there are only two supports, degeneracy is not possible. If there are three supports, the conditions summarized in the previous section are applied.

Finally, for generality, the case of improper Newton Diagrams should be considered. Arnold [19] has suggested that in this case one can "close" the Newton diagram by artificially adding monomials $x_1^{p_1}$ and/or $x_2^{p_2}$ where needed, taking p_1 and p_2 sufficiently large. As an illustration consider the polynomial

$$g(u,v) = u^3 + u^2v + uv^2 \quad . \tag{33}$$

The corresponding Newton diagram with three supports is portrayed on Fig. 3. The Newton diagram is clearly improper (there is no monomial involving v only). Thus consider

$$\tilde{g}(u,v) = u^3 + u^2v + uv^2 + v^\delta \tag{34}$$

where δ is sufficiently large. The Newton number of this polynomial is:

$$\begin{aligned} \nu(\tilde{g}) &= 2S_{\tilde{g}} - \delta - 3 + 1 \\ &= 2\left(\frac{\delta-2}{2} + 2 + 2\right) - \delta - 3 + 1 = 4 \end{aligned} \tag{35}$$

independent of δ. Then $\nu(g) = \nu(\tilde{g}) = 4$.

APPLICATION 1: REACTION BETWEEN TWO ADSORBED SPECIES

Consider the reaction sequence:

$$\begin{aligned} A + S' &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} AS' \\ B + S' &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} BS' \\ AS' + BS' &\xrightarrow{k_5} AB + 2S' \end{aligned} \tag{36}$$

taking place in an isothermal, isobaric CSTR of residence time τ. Assuming mass action kinetics and introducing the dimensionless variables and parameters defined in the Nomenclature, the steady-state balances are

$$-\tilde{\alpha}_1\tilde{x}_1(1-\tilde{x}_3-\tilde{x}_4)+\tilde{\alpha}_2\tilde{x}_3-(\tilde{x}_1-u_1)=0 \tag{37.1}$$

$$-\tilde{\alpha}_3\tilde{x}_2(1-\tilde{x}_3-\tilde{x}_4)+\tilde{\alpha}_4\tilde{x}_4-(\tilde{x}_2-u_2)=0 \tag{37.2}$$

$$\tilde{\alpha}_1\tilde{x}_1(1-\tilde{x}_3-\tilde{x}_4)-\tilde{\alpha}_2\tilde{x}_3-\tilde{\alpha}_5\tilde{x}_3\tilde{x}_4=0 \tag{37.3}$$

$$\tilde{\alpha}_3\tilde{x}_2(1-\tilde{x}_3-\tilde{x}_4)-\tilde{\alpha}_4\tilde{x}_4-\tilde{\alpha}_5\tilde{x}_3\tilde{x}_4=0 \tag{37.4}$$

The first two equations may be solved in terms of $\tilde{x}_1$ and $\tilde{x}_2$ to obtain

$$\tilde{x}_1=\frac{u_1+\tilde{\alpha}_2\tilde{x}_3}{1+\tilde{\alpha}_1(1-\tilde{x}_3-\tilde{x}_4)} \tag{38}$$

$$\tilde{x}_2=\frac{u_2+\tilde{\alpha}_4\tilde{x}_4}{1+\tilde{\alpha}_3(1-\tilde{x}_3-\tilde{x}_4)} \tag{39}$$

Substituting these formulae in the last two steady-state equations (37.3 and 37.4) and defining deviation variables from a solution $(\tilde{x}_{30},\tilde{x}_{40})$ of these two equations

$$\nabla_1=\tilde{x}_3-\tilde{x}_{30}$$

$$\nabla_2=\tilde{x}_4-\tilde{x}_{40}\ ,$$

one obtains

$$h_1(\nabla_1,\nabla_2)=h_{11}\nabla_1+h_{12}\nabla_2+h_{15}\nabla_1\nabla_2+h_{13}\nabla_1^2+h_{14}\nabla_2^2+h_{16}\nabla_1^2\nabla_2+h_{17}\nabla_1\nabla_2^2=0 \tag{40.1}$$

$$h_2(\nabla_1,\nabla_2)=h_{21}\nabla_1+h_{22}\nabla_2+h_{25}\nabla_1\nabla_2+h_{23}\nabla_1^2+h_{24}\nabla_2^2+h_{26}\nabla_1^2\nabla_2+h_{27}\nabla_1\nabla_2^2\ , \tag{40.2}$$

where the h_{ij} are defined in the Appendix.

The supports of the Newton diagrams for h_1 and h_2 are given in Fig. 4 for the case in which none of the h_{ij} are zero. Depending on the values of the parameters u_1, u_2, $\tilde{\alpha}_1$, $\tilde{\alpha}_2$, $\tilde{\alpha}_3$, $\tilde{\alpha}_4$, and $\tilde{\alpha}_5$, some of the coefficients of the supports may vanish. Then, formula (32) can be used to determine the Newton number of the steady-state solution in each case. The multiplicity of the steady-state $(\tilde{x}_{30}, \tilde{x}_{40})$ will then be greater than or equal to the Newton number. The multiplicity will be greater than the Newton number only in the case of degeneracy.

Table 1 summarizes all the possibilities. In each case the Newton diagrams of h_1, h_2 and $h_1 \cdot h_2$ are presented and the corresponding degeneracy conditions are given. If, for example, the system parameters are such that case H in Table 1 is observed, the multiplicity is 2 unless

$$\text{(i)} \quad 4h_{23}h_{24} - h_{25}^2 = 0 \tag{41}$$

or

$$\text{(ii)} \quad h_{25}(h_{11}h_{12}h_{25} + h_{12}^2 h_{23} + h_{11}^2 h_{24}) = 0 \tag{42}$$

are satisfied. Condition (41) is obtained if the Newton diagram for h_2 is degenerate while condition (42) is obtained if the Newton diagram for $h_1 \cdot h_2$ is degenerate. If either Eqn. (41) or (42) is satisfied, multiplicity of the steady state is greater than two.

As a particular example, consider $u_1 = u_2 = 1$ and parameter values $\tilde{\alpha}_1$, $\tilde{\alpha}_2$, $\tilde{\alpha}_3$, $\tilde{\alpha}_4$, and $\tilde{\alpha}_5$ such that the steady-state solution is $\tilde{x}_{30} = \tilde{x}_{40} = 0.1$. This implies that the parameters $\tilde{\alpha}_1$ must satisfy the equations:

$$0.8\tilde{\alpha}_1 - 0.1\tilde{\alpha}_2 - 0.01\tilde{\alpha}_5 - 0.008\tilde{\alpha}_1\tilde{\alpha}_5 = 0 \tag{43.1}$$

and

$$0.8\tilde{\alpha}_3 - 0.1\tilde{\alpha}_4 - 0.01\tilde{\alpha}_5 - 0.008\tilde{\alpha}_3\tilde{\alpha}_5 = 0 \quad . \tag{43.2}$$

The coefficients h_{ij} take on specific values by substituting $x_{30} = x_{40} = 0.1$ in the equations for h_{ij} in the Appendix. Since all the $\tilde{\alpha}_i$ must be positive, one can see that h_{11}, h_{12}, h_{21}, h_{22} are all different from zero for all admissible α_i (>0). Then the Newton number is 1 (case A in Table 1). The degeneracy condition in this case is:

$$h_{11} \cdot h_{22} - h_{12} \cdot h_{21} = 0 \tag{44}$$

or

$$\alpha_4(\alpha_1 + 0.07\alpha_1\alpha_5 + 0.1\alpha_5) + (\alpha_2 + 0.01\alpha_1\alpha_5)(\alpha_3 + 0.07\alpha_3\alpha_5 + 0.1\alpha_5 + \alpha_4) \tag{45}$$

which is not possible for positive $\tilde{\alpha}_i$. Thus the multiplicity of the steady state is definitely one, meaning that bifurcation from the steady state $x_{30} = x_{40} = 0.1$ is not observed for any positive $\tilde{\alpha}_i$.

Multiplicity with Feedback Control

Steady-state multiplicity may be obtained in a chemical reaction system as a result of the introduction of a feedback controller (e.g., Ref. 16). The Newton diagram approach is particularly useful for determining the feedback parameter values at which multiplicity (bifurcation) of steady states is observed.

Returning to the particular case considered in Eqns. (43) above, assume now that the feed concentration of A is manipulated according to the measurement of the concentrations of A and B in the reactor effluent according to

$$u_1 = u_{10} + b_1(x_1 - x_{10}) + b_2(x_2 - x_{20}) \quad . \tag{46}$$

The steady-state equations become

$$-\tilde{\alpha}_1\tilde{x}_1(1 - \tilde{x}_3 - \tilde{x}_4) + \tilde{\alpha}_2\tilde{x}_3 - \left(\tilde{x}_1 - u_{10} - b_1(\tilde{x}_1 - \tilde{x}_{10}) - b_2(\tilde{x}_2 - \tilde{x}_{10})\right) = 0 \tag{47.1}$$

$$-\tilde{\alpha}_3\tilde{x}_2(1 - \tilde{x}_3 - \tilde{x}_4) + \tilde{\alpha}_4\tilde{x}_4 - (\tilde{x}_2 - u_2) = 0 \tag{47.2}$$

$$\bar{a}_1\bar{x}_1(1-\bar{x}_3-\bar{x}_4) - \bar{a}_2\bar{x}_3 - \bar{a}_5\bar{x}_3\bar{x}_4 = 0 \tag{47.3}$$

$$\bar{a}_3\bar{x}_2(1-\bar{x}_3-\bar{x}_4) - \bar{a}_4\bar{x}_4 - \bar{a}_5\bar{x}_3\bar{x}_4 = 0 \ . \tag{47.4}$$

Defining deviation variables

$$\phi_1 = \bar{x}_1 - \bar{x}_{10} \ , \ \phi_2 = \bar{x}_2 - \bar{x}_{20} \ , \ \phi_3 = \bar{x}_3 - \bar{x}_{30} \ , \ \phi_4 = \bar{x}_4 - \bar{x}_{40} \tag{48}$$

and solving Eqns. (47.1) and (47.2) for ϕ_1 and ϕ_2 in terms of ϕ_3 and ϕ_4 yields

$$\phi_2 = \frac{\bar{a}_3\bar{x}_{20}(\phi_3+\phi_4) + \bar{a}_4\phi_4}{1+\bar{a}_3(1-\bar{x}_{30}-\bar{x}_{40}-\phi_3-\phi_4)} \tag{49.1}$$

$$\phi_1 = \frac{\bar{a}_1\bar{x}_{10}(\phi_3+\phi_4) + \dfrac{(\bar{a}_2+b_2)[\bar{a}_3\bar{x}_{20}(\phi_3+\phi_4)+\bar{a}_4\phi_4]}{1+\bar{a}_3(1-\bar{x}_{30}-\bar{x}_{40}-\phi_3-\phi_4)}}{1-b_1+\bar{a}_1(1-\bar{x}_{30}-\bar{x}_{40}-\phi_3-\phi_4)} \ . \tag{49.2}$$

Assume now $u_{10} = u_2 = \bar{a}_1 = \bar{a}_2 = \bar{a}_3 = \bar{a}_4 = 1$ and $\bar{a}_5 = 350/9$. Eqns. (43) are then satisfied for $\bar{x}_{30} = \bar{x}_{40} = 0.1$ whereas $\bar{x}_{10} = \bar{x}_{20} = 11/18$. Next, ϕ_1 and ϕ_2 are found from Eqns. (49) in terms of only b_1 and b_2, and substitution of these formulae in the last two steady-state equations gives

$$\begin{aligned}
\bar{h}_1(\phi_3,\phi_4) = {} & [-2337.32+1312b_1+8.8b_2]\phi_3 \\
& +[-224.16+145.8b_1+23.2b_2]\phi_4 \\
& +[1873.4-729b_1-11b_2]\phi_3^2 \\
& +[171.6-81b_1-29b_2]\phi_4^2 \\
& +[-258.2+450b_1-40b_2]\phi_3\phi_4 \\
& -740\phi_3^3-92\phi_4^3+[1750-700b_1]\phi_3^2\phi_4 \\
& +[1102-700b_1]\phi_3\phi_4^2-700\phi_3^3\phi_4-700\phi_3\phi_4^3 = 0
\end{aligned} \tag{50.1}$$

and

$$\tilde{h}_2(\phi_3,\phi_4) = -137\phi_3 - 155\phi_4 + 70\phi_3^2 + 70\phi_4^2 + 41\phi_3\phi_4 + 700\phi_3\phi_4^2 + 700\phi_3^2\phi_4 = 0 \quad . \tag{50.2}$$

The Newton diagram of $\tilde{h}_2(\phi_3,\phi_4)$ has supports at $(\phi_3,\phi_4) = (0,1)$ and $(\phi_3,\phi_4) = (1,0)$. Consequently, in order to have multiplicity different from 1, it is necessary that the coefficients of ϕ_3 and ϕ_4 in $h_1(\phi_3,\phi_4)$ vanish.* That is,

$$-2337.32 + 1312b_1 + 8.8b_2 = 0 \tag{51.1}$$

$$-224.16 + 145.8b_1 + 23.2b_2 = 0 \quad . \tag{51.2}$$

These equations are solved to find $b_1 = 1.7922$; $b_2 = -1.6012$ For these values of b_1 and b_2 the function $h_1(\phi_3,\phi_4)$ becomes

$$\tilde{h}_1(\phi_3,\phi_4) = 584.499\phi_3^2 + 72.867\,\phi_4^2 + 612.338\phi_3\phi_4 - 740\phi_3^2 - 92\phi_4^2 + 495.460\phi_3^2\phi_4 - 152.540\phi_3\phi_4^2 - 700\phi_3^3\phi_4 - 700\phi_3\phi_4^3 \quad . \tag{52}$$

The Newton diagrams for $\tilde{h}_1$, $\tilde{h}_2$ and $\tilde{h}_1 \cdot \tilde{h}_2$ are presented in Fig. 5. It is clear that the Newton number is

$$\nu = \min(1\cdot 2, 2\cdot 1) = 2 \quad . \tag{53}$$

Degeneracy is possible due to $\tilde{h}_1$ and $\tilde{h}_1 \cdot \tilde{h}_2$. The degeneracy conditions here are:

$$\text{(i)} \quad (612.338)^2 - 4(584.499)(72.867) = 0 \quad \text{for } \tilde{h}_1 \tag{54.1}$$

and

$$\text{(ii)} \quad (80{,}076.36)(104{,}895.17) - (11{,}298.39)(174{,}487.651) = 0 \quad \text{for } \tilde{h}_1 \cdot \tilde{h}_2 \quad . \tag{54.2}$$

Since neither of Eqns. (54) is satisfied, degeneracy is not possible, and the multiplicity of the steady-state solution is two for $b_1 = 1.7922$ and $b_2 = -1.6012$ Thus, it is seen in this example that feedback may produce bifurcation of the steady-state solution.

* Multiplicity due to degeneracy is also possible along the line $b_2 = 101.072\, b_1 - 182.746$.

APPLICATION 2: STEADY-STATE MULTIPLICITY FOR TWO AND THREE PARALLEL IRREVERSIBLE REACTIONS OF ARBITRARY ORDER IN A CSTR

1. Two Reactions

Consider the reactions

$$A' \xrightarrow{\hat{k}_1} C$$

$$B' \xrightarrow{\hat{k}_2} D \qquad (55)$$

taking place in an adiabatic CSTR. Assume the first reaction is of $\tilde{n}$-th order and the second is of $\tilde{m}$-th order. The mass and energy balances for the CSTR system may be written in dimensionless form as

$$1 - u_A - Da_1 \cdot u_A^{\tilde{n}} \cdot X_1 = 0 \qquad (56.1)$$

$$1 - u_B - Da_2 \cdot u_B^{\tilde{m}} \cdot X_2 = 0 \qquad (56.2)$$

$$1 - y + \beta_A \cdot Da_1 \cdot u_A^{\tilde{n}} X_1 + \beta_B \cdot Da_2 \cdot u_B^{\tilde{m}} X_2 = 0 \qquad (56.3)$$

Definitions of all dimensionless quantities are given in the Nomenclature.

Multiplying Eqn. (56.1) by β_A, Eqn. (56.2) by β_B, adding to Eqn. (56.3), and solving for y yields

$$y = \beta_A(1 - u_A) + \beta_B(1 - u_B) + 1 \qquad (57)$$

Substituting for y in Eqn. (56) gives two nonlinear equations for u_A and u_B:

$$1 - u_A - Da_1 u_A^{\tilde{n}} e^{\gamma_1'}\left(1 - \frac{1}{1 + \beta_A(1 - u_A) + \beta_B(1 - u_B)}\right) = 0 \qquad (58.1)$$

$$1 - u_B - Da_2 u_B^{\tilde{m}} e^{\gamma_2'}\left(1 - \frac{1}{1 + \beta_A(1 - u_A) + \beta_B(1 - u_B)}\right) = 0 \qquad (58.2)$$

Assume now (u_{AS}, u_{BS}) is a solution to Eqns. (58). Taylor expanding the exponential terms around (u_{AS}, u_{BS}) and introducing deviation variables

$$\eta_1 = u_A - u_{AS} \quad ; \quad \eta_2 = u_B - u_{BS} \quad , \tag{59}$$

Eqns. (58) may be rewritten in the form

$$\tilde{h}_1(\eta_1,\eta_2) = \tilde{h}'_{11}\,\eta_1 + \tilde{h}'_{12}\,\eta_2 + O(\eta^2) \tag{60.1}$$

$$\tilde{h}_2(\eta_1,\eta_2) = \tilde{h}'_{21}\,\eta_1 + \tilde{h}'_{22}\,\eta_2 + O(\eta^2) \tag{60.2}$$

where $\tilde{h}'_{ij}$ are given in the Appendix.

From the Bernshtein Theorem and Newton polyhedra for this system, since $\tilde{h}'_{12}$, $\tilde{h}'_{21}$ cannot be zero (this requires u_{AS} or $u_{BS} = 1$ which is not possible for nonzero rate constants), steady-state bifurcation is possible only because of degeneracy. If $\tilde{h}'_{11}$ and/or $\tilde{h}'_{22}$ are zero, (1,1) is a support and, since the Newton diagram of $\tilde{h}_1 \cdot \tilde{h}_2$ consists of two faces each having two supports, degeneracy is not possible. Thus degeneracy is possible only when $\tilde{h}'_{11} \cdot \tilde{h}'_{22} \neq 0$. In this case, degeneracy occurs only if

$$\tilde{h}'_{11} \cdot \tilde{h}'_{22} - \tilde{h}'_{12} \cdot \tilde{h}'_{21} = 0 \tag{61}$$

which is the same as the condition that the determinant of the Jacobian be zero

Employing the expressions for $\tilde{h}'_{ij}$ in the Appendix, Eqn. (61) may be written

$$\begin{aligned} & u_{BS}[-u_{AS} - \tilde{n}(1-u_{AS})][(1-u_{BS})\gamma_2' \beta_B] \\ & + u_{AS}[-u_{BS} - \tilde{m}(1-u_{BS})][(1-u_{AS})\gamma_1' \beta_A] \\ & + [1 + \tilde{n}(1-u_{AS})][1+\tilde{m}(1-u_{BS})][1 + \beta_A(1-u_{AS}) + \beta_B(1-u_{BS})]^2 = 0 \quad . \end{aligned} \tag{62}$$

This equation together with the steady-state equations (58) may be solved simultaneously for u_{AS}, u_{BS} and one parameter chosen as the bifurcation parameter.

If, for example, one sets $\bar{n} = 2$, $\bar{m} = 3$, $Da_1 = Da_2 = 0.1$, $\gamma_1' = 20$, $\gamma_2' = 10$, $\beta_A = 1$, leaving β_B free, numerical solution of Eqns. (50) and (63) for u_{AS}, u_{BS} and β_B gives

$$u_{AS} = 0.8622 \quad , \quad u_{BS} = 0.9006 \quad , \quad \beta_B = -1.066 \quad . \tag{63}$$

Consequently for the reaction system with the given parameter values steady-state bifurcation occurs for $\beta_B = -1.066$. Numerical simulations show that the steady-state is unique for $\beta_B > -1.066$, whereas for $\beta_B < -1.066$, there are three steady states. Thus, the multiplicity of the steady state $(u_{AS}, u_{BS}) = (0.8622, 0.9006)$ is 3 which is greater than the Newton number of unity because of degeneracy.

2. Three Reactions

Consider now the case of three parallel reactions of arbitrary order:

$$\begin{aligned} A' &\xrightarrow{\hat{k}_1} C \\ B' &\xrightarrow{\hat{k}_2} D \\ E' &\xrightarrow{\hat{k}_3} F' \end{aligned} \tag{64}$$

In this case, after eliminating y as above, the steady-state equations are given by

$$1 - u_A - Da_1 u_A^{\bar{n}} e^{\gamma_1'\left(1 - \frac{1}{1 + \beta_A(1-u_A) + \beta_B(1-u_B) + \beta_E(1-u_E)}\right)} = 0 \tag{65.1}$$

$$1 - u_B - Da_2 u_B^{\bar{m}} e^{\gamma_2'\left(1 - \frac{1}{1 + \beta_A(1-u_A) + \beta_B(1-u_B) + \beta_E(1-u_E)}\right)} = 0 \tag{65.2}$$

$$1 - u_E - Da_3 u_E^{\tilde{\ell}} e^{\gamma_3'} \left(1 - \frac{1}{1 + \beta_A(1-u_A) + \beta_B(1-u_B) + \beta_E(1-u_E)}\right) = 0 \qquad (65.3)$$

Expanding the exponential terms and introducing deviation variables as before ($\eta_3 = u_E - u_{Es}$), Eqns. (65) become

$$\tilde{h}_1'(\eta_1,\eta_2,\eta_3) = \tilde{h}_{11}'\eta_1 + \tilde{h}_{12}'\eta_2 + \tilde{h}_{13}'\eta_3 + O(\eta^2) \qquad (66.1)$$

$$\tilde{h}_2'(\eta_1,\eta_2,\eta_3) = \tilde{h}_{21}'\eta_1 + \tilde{h}_{22}'\eta_2 + \tilde{h}_{23}'\eta_3 + O(\eta^2) \qquad (66.2)$$

$$\tilde{h}_3'(\eta_1,\eta_2,\eta_3) = \tilde{h}_{31}'\eta_1 + \tilde{h}_{32}'\eta_2 + \tilde{h}_{33}'\eta_3 + O(\eta^3) \qquad (66.3)$$

where again the $\tilde{h}_{ij}'$ are explicitly evaluated in the Appendix.

If all the $\tilde{h}_{ij}'$ are not zero then a sufficient condition for absence of bifurcation at the reference steady state may be obtained. Fig. 7 summarizes the Newton diagrams in this case. Equation (12) in this case becomes

$$v = U = V_3(S_1) + V_3(S_2) + V_3(S_3) - V_3(S_1+S_2) - V_3(S_1+S_3) - V_3(S_2+S_3) + V_3(S_1+S_2+S_3). \qquad (67.1)$$

Now

$$\left.\begin{aligned} &V_3(S_1) = V_3(S_2) = V_3(S_3) = \tfrac{1}{3}\cdot\tfrac{1}{2}\cdot 1\cdot 1\cdot 1 = \tfrac{1}{6} \\ &V_3(S_1+S_2) - V_3(S_1+S_3) = V_3(S_2+S_3) = \tfrac{1}{3}\cdot\tfrac{1}{2}\cdot 2\cdot 2\cdot 2 = \tfrac{8}{6} \\ &V_3(S_1+S_2+S_3) = \tfrac{1}{3}\cdot\tfrac{1}{2}\cdot 3\cdot 3\cdot 3 = \tfrac{27}{6} \end{aligned}\right\} \qquad (67.2)$$

Substituting in Eqn. (67.1) gives

$$= \tfrac{1}{6} + \tfrac{1}{6} + \tfrac{1}{6} - \tfrac{8}{6} - \tfrac{8}{6} - \tfrac{8}{6} + \tfrac{27}{6} = \tfrac{6}{6} = 1 \quad .$$

Thus the Newton number is 1, and, unless degeneracy occurs, the multiplicity of

the root (u_{AS}, u_{BS}, u_{ES}) is 1. Bifurcation to multiple steady states from this steady state does not occur, therefore, without degeneracy.

Next, conditions for degeneracy are considered. From Fig. 7B it is evident that there are six supports at positions (2,0,0), (0,2,0), (0,0,2), (1,1,0), (1,0,1) and (0,1,1). The degeneracy condition (22) for $\tilde{h}_i, \tilde{h}_j$ in this case becomes:

$$\left(\frac{\alpha_0}{d_0}\right)^{d_0}\left(\frac{\alpha_1}{d_1}\right)^{d_1}\left(\frac{\alpha_2}{d_2}\right)^{d_2}\left(\frac{\alpha_3}{d_3}\right)^{d_3}\left(\frac{\alpha_4}{d_4}\right)^{d_4}\left(\frac{\alpha_5}{d_5}\right)^{d_5} = 1, \tag{68}$$

where α_i are the coefficients of the supports on the Newton diagrams, and $d_0,\ldots,d_5$ satisfy

$$\begin{aligned} 2d_2 + d_3 + d_4 &= 0 \\ 2d_1 + d_3 + d_5 &= 0 \\ 2d_0 + d_4 + d_5 &= 0 \end{aligned} \tag{69}$$

and are integers prime to each other. The obvious choice is $d_0 = d_1 = d_2 = 1$ $d_3 = d_5 = d_5 = -1$.

Therefore Eqn. (68) becomes:

$$\alpha_0\alpha_1\alpha_2 + \alpha_3\alpha_4\alpha_5 = 0 \tag{70}$$

or

$$\tilde{h}'_{i3}\,\tilde{h}'_{j3}\,\tilde{h}'_{i1}\,\tilde{h}'_{j1}\,\tilde{h}'_{i2}\,\tilde{h}'_{j2} + \left(\tilde{h}'_{i1}\,\tilde{h}'_{j3} + \tilde{h}'_{i3}\,\tilde{h}'_{j1}\right)\left(\tilde{h}'_{i2}\,\tilde{h}'_{j3} + \tilde{h}'_{i3}\,\tilde{h}'_{j2}\right) \cdot \left(\tilde{h}'_{i1}\,\tilde{h}'_{j2} + \tilde{h}'_{i2}\,\tilde{h}'_{j1}\right) = 0 \; ; \quad (i,j) = (1,2),(1,3),(2,3) \; . \tag{(}$$

Thus we obtain three degeneracy conditions. If any of these is satisfied, the steady state is not unique.

Considering next possible degeneracy of $\bar{h}_1 \cdot \bar{h}_2 \cdot \bar{h}_3$, there are 10 supports in Fig. 7C: (3,0,0), (0,3,0), (0,0,3), (2,1,0), (2,0,1), (1,0,2), (1,2,0), (0,1,2), (0,2,1) and (1,1,1). Condition (22) becomes:

$$\prod_{i=0}^{9} \left(\frac{a_i}{d_i}\right)^{d_i} = 1 \quad , \tag{72}$$

where

$$\begin{aligned} d_9 + 3d_0 + 2d_3 + 2d_4 + d_5 + d_6 &= 0 \\ d_9 + 3d_1 + 2d_6 + 2d_8 + d_3 + d_7 &= 0 \\ d_9 + 3d_2 + 2d_5 + 2d_7 + d_4 + d_8 &= 0 \end{aligned} \tag{73}$$

which are satisfied by the prime integers $d_3 = d_4 = d_5 = d_6 = d_7 = d_8 = 1$, $d_0 = d_1 = d_2 = -1$, $d_9 = -3$. Substituting these values in Eqn. (72) gives the degeneracy condition

$$27a_3a_4a_5a_6a_7a_8 - a_0a_1a_2a_9^3 = 0 \quad , \tag{74}$$

with

$$\begin{aligned} a_0 &= \bar{h}'_{11}\,\bar{h}'_{21}\,\bar{h}'_{31} & a_5 &= \sum \bar{h}'_{12}\,\bar{h}'_{j2}\,\bar{h}'_{k3} \\ a_1 &= \bar{h}'_{12}\,\bar{h}'_{22}\,\bar{h}'_{32} & a_6 &= \sum \bar{h}'_{13}\,\bar{h}'_{j3}\,\bar{h}'_{k2} \\ a_2 &= \bar{h}'_{13}\,\bar{h}'_{23}\,\bar{h}'_{33} & a_7 &= \sum \bar{h}'_{11}\,\bar{h}'_{j1}\,\bar{h}'_{k2} \\ a_3 &= \sum \bar{h}'_{11}\,\bar{h}'_{j1}\,\bar{h}'_{k2} & a_8 &= \sum \bar{h}'_{13}\,\bar{h}'_{j3}\,\bar{h}'_{k1} \\ a_4 &= \sum \bar{h}'_{12}\,\bar{h}'_{j2}\,\bar{h}'_{k1} & a_9 &= \sum \bar{h}'_{11}\,\bar{h}'_{j2}\,\bar{h}'_{k3} \end{aligned} \tag{75}$$

where the indicated sums are over all possible triplets (i,j,k);- i,j,k = 1,2,3.

Hence, unless one of the Conditions (71) or (74) is satisfied, the solution (u_{AS}, u_{BS}, u_{ES}) is unique when all of the $\bar{h}'_{ij}$ are nonzero. If, on the other hand, one of Eqns. (71) and (74) is satisfied for some parameter values,

then steady-state bifurcation is guaranteed for these parameter values. If some of the $\tilde{h}'_{ij}$ vanish, the Newton diagrams must be constructed for the case involved, and degeneracy conditions must be obtained on every face of the Newton frontier.

CONCLUSIONS

The Newton polygon approach is a very powerful method of determining the points in the parameter space at which steady-state bifurcation occurs. It is an extremely simple method in the case of two algebraic equations, since only a simple geometrical construction is required. The method as presented is general and applies for any number of steady-state equations. If the system cannot be reduced to less than four algebraic equations, there are practical limitations since it is hard to visualize a Newton polyhedron in four or higher dimensions. Still, in such a case, methods of algebraic geometry may be used. Keller's approach [13] is likely the method of choice for such problems.

For systems that can be reduced to two or three equations, the Newton diagram analysis has another major advantage. Steady-state multiplicity depends only on the supports on the Newton frontier, that is, on certain leading order monomials in the steady-state equations. Unless degeneracy occurs, the coefficients of the supports do not matter: only the structure of the equations, as represented by the Newton frontier supports, influence multiplicity. All systems that possess the same Newton frontiers have the same underlying structure. Differences in "higher order terms" (i.e., in monomials corresponding to supports not in the Newton frontier) do not alter the multiplicity properties of the singularity under study. Thus the Newton frontiers provide a normal form for a general class of algebraic systems.

In the Newton polygon approach, one does not need to choose *a priori* a bifurcation parameter since the conditions for bifurcation are written in terms of all system parameters, thus defining a hyperplane in the parameter space along which the bifurcation occurs. One can then easily see which individual parameter is a convenient choice for a bifurcation parameter for computational studies or other analyses. This property is particularly importa for purposes of design as in the case of a system with feedback. The method should contribute significantly to analysis of steady-state multiplicity in chemical engineering systems.

NOMENCLATURE

α_{ni}	coefficient of monomials in Eqn. (2)
A,B,AB	chemical species in Application 1
A',B',C,D,E',F'	chemical species in Application 2
b_1, b_2	feedback parameters in Eqn. (46)
C_i	concentration of species i in Application 1 (mole/cm^3)
C_0	maximum possible concentration of adsorbed species in Application 1 (mole/cm^3)
$\tilde{C}_i$	concentration of species i in Application 2 (mole/cm^3)
C_p	specific heat capacity in Application 2 $\left(\frac{cal}{mole \cdot cm^3}\right)$
d_0-d_k	sequence defined in Eqn. (18)
$Da_i = \frac{V'\hat{k}_i(Tm)}{\tilde{q}} \tilde{C}_{i0}^{\tilde{n}-1}$	; Damköhler numbers in Application 2
E_i	activation energies in Application 2 (cal/mole)
f_i	functions defined in Eqn. (1)
$f_{i\Delta}$	defined in Eqn. (17)
g	defined in Eqn. (33)
$\tilde{g}$	defined in Eqn. (34)
$\tilde{g}_1, \tilde{g}_2$	defined in Eqn. (25)
g_1, g_2	defined in Eqn. (24)
H	enthalpy (cal/mole) in Application 2; $H = \frac{U_a}{\tilde{q}\rho c_p}$
h_1, h_2	defined in Eqns. (40)
h_{1j}	defined in the Appendix
$\tilde{h}_1, \tilde{h}_2$	defined in Eqns. (50)
$\tilde{h}_1', \tilde{h}_2'$	defined in Eqns. (60)

$\tilde{h}'_{ij}$	defined in the Appendix
k	dimension of system (1)
k_i	rate constants in Application 1 (appropriate units)
$\hat{k}_i$	rate constants in Application 2 (appropriate units)
$\tilde{l},\tilde{m},\tilde{n}$	orders of reaction in Application 2
L	Lagrange function defined in Eqn. (19)
m_i	defined in Eqn. (17)
p_i	powers of monomials
q	flow rate in Application 2 (mole/sec)
r_1	$k_1 C_A(C_0 - C_{AS'} - C_{BS'}) - k_2 C_{AS'}$ (Appl. 1)
r_2	$k_3 C_B(C_0 - C_{AS'} - C_{BS'}) - k_4 C_{AS'}$ (Appl. 1)
r_3	$k_5 C_{AS'} C_{BS'}$ (Appl. 1)
R^n	n-dimensional space of real numbers
S_i	defined in Eqn. (12)
s	dimension (Δ)
S	areas under Newton polygon
S'	catalytic site in Appl. 1
t	time (sec)
T	temperature in Appl. 2 (^{0}C)
$T_m = \frac{T_0 + HT_c}{1+H}$	reference temperature in appl. 2 (^{0}C)
U	mixed Minkowski volume defined in Eqn. (12)
$u_A, u_B, u_E = \frac{C_i}{C_{i0}}$	dimensionless concentrations in Appl. 2
u_{AS}, u_{BS}, u_{ES}	steady-state dimensionless concentrations in Appl. 2
u_1, u_2, u_{10}	feed concentrations (dimensionless) in Appl. 1; $u_1 = \frac{u_A}{C_0}$, $u_2 = \frac{u_B}{C_0}$

U_a heat transfer coefficient in Application 2 (cal/mole ^0C)

V volume of subdomain of positive orthant

V_k defined in Eqn. (8)

$V_{j\ell}$ defined in Eqn. (8)

V' reactor volume in Application 2 (cm^3)

x monomial in Eqn. (2)

x_i deviation variables in Eqn. (2)

$\tilde{x}_1$-$\tilde{x}_4$ dimensionless concentrations in Appl. 1; $\tilde{x}_i = \frac{C_i}{C_0}$

$X_i = \frac{\hat{k}_i(T)}{\hat{k}_i(T_m)} = e^{\gamma_i'(1-\frac{1}{y})}$; dimensionless rate constants in Appl. 2

$y = \frac{T}{T_m}$ dimensionless temperature in Appl. 2

Z^k k dimensional set of integers

Z_i monomials in Eqn. (19)

Greek Symbols

$\alpha, \alpha_1, \alpha_2$ powers of monomials x_k

$\tilde{\alpha}_1$-$\tilde{\alpha}_5$ dimensionless rate constants in Appl. 1: $\tilde{\alpha}_1 = k_1 C_0 \tau$,
$\tilde{\alpha}_2 = k_2 \tau$, $\tilde{\alpha}_3 = k_3 C_0 \tau$, $\tilde{\alpha}_4 = k_4 \tau$, $\tilde{\alpha}_5 = k_5 C_0 \tau$

β, β_1, β_2 powers of monomials x_k

$\beta_A, \beta_B, \beta_E$ dimensionless heats of reaction in Appl. 2: $\beta_i = \frac{(-\Delta H_i) C_{i0}}{\rho c_p T_m (1+$

γ_i dimensionless activation energies in Appl. 2; $\gamma_i = \frac{E_i}{RT_m}$

$\tilde{\Gamma}_-$ convex envelope defined in text

$\tilde{\Gamma}$ Newton frontier

δ parameter in illustrative example (Eqn. 3)

Δ	face of Newton frontier
ΔH_i	heats of reaction in Appl. 2 (cal/mole)
η_1, η_2, η_3	deviation variables in Appl. 2
$\theta = \frac{t}{\tau}$	dimensionless time in Appl. 1
λ	Lagrange multiplier
μ	Milnor number
ν	Newton number
ξ_i	variables in Eqn. (1)
ρ	density in Appl. 2 (mole/cm^3)
τ	reactor residence time in Appl. 1 (sec)
ϕ_i	deviation variables in Appl. 1

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APPENDIX

The h_{ij} in Eqn. (40) are:

$$h_{11} = -u_1\tilde{\alpha}_1 - \tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{40} + 2\tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{40}^2 - \tilde{\alpha}_2 - \tilde{\alpha}_5\tilde{x}_{40}$$

$$h_{12} = -u_1\tilde{\alpha}_1 - \tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{30} + 2\tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{30}\tilde{x}_{40} + \tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{30}^2 - \tilde{\alpha}_5\tilde{x}_{30}$$

$$h_{13} = \tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{40}$$

$$h_{14} = \tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{30}$$

$$h_{15} = -\tilde{\alpha}_1\tilde{\alpha}_5 + 2\tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{30} + 2\tilde{\alpha}_1\tilde{\alpha}_5\tilde{x}_{40} - \tilde{\alpha}_5$$

$$h_{16} = \tilde{\alpha}_1\tilde{\alpha}_5$$

$$h_{17} = \tilde{\alpha}_1\tilde{\alpha}_5$$

$$h_{21} = -u_2\tilde{\alpha}_3 - \tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{40} + 2\tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{30}\tilde{x}_{40} + \tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{40}^2 - \tilde{\alpha}_5\tilde{x}_{40}$$

$$h_{22} = -u_2\tilde{\alpha}_3 - \alpha_3\tilde{\alpha}_5\tilde{x}_{30} + \tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{30}^2 + 2\tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{30}\tilde{x}_{40} - \tilde{\alpha}_4 - \tilde{\alpha}_5\tilde{x}_{30}$$

$$h_{23} = \tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{40}$$

$$h_{24} = \tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{30}$$

$$h_{25} = -\tilde{\alpha}_3\tilde{\alpha}_5 + 2\tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{30} + 2\tilde{\alpha}_3\tilde{\alpha}_5\tilde{x}_{40} - \tilde{\alpha}_5$$

$$h_{26} = \tilde{\alpha}_3\tilde{\alpha}_5$$

$$h_{27} = \tilde{\alpha}_3\tilde{\alpha}_5$$

The $\tilde{h}'_{1j}$ in Eqns. (60) are given by:

$$\tilde{h}'_{11} = -1 - \frac{\tilde{n}(1 - u_{AS})}{u_{AS}} + \frac{\gamma'_1\beta_A(1 - u_{AS})}{\delta^2}$$

$$\tilde{h}'_{12} = \frac{\gamma'_1\beta_B(1 - u_{AS})}{\delta^2}$$

$$\tilde{h}_{21}' = \frac{\gamma_2'\beta_A(1-u_{BS})}{\delta^2}$$

$$\tilde{h}_{22}' = -1 - \frac{\tilde{m}(1-u_{BS})}{u_{BS}} + \frac{\gamma_2'\beta_B(1-u_{BS})}{\delta^2}$$

where $\delta = 1 + \beta_A(1-u_{AS}) + \beta_B(1-u_{BS})$.

The h_{ij}' in Eqns. (66) are given by:

$$\tilde{h}_{11}' = -1 - \frac{\tilde{n}(1-u_{AS})}{u_{AS}} + \frac{\gamma_1'\beta_A(1-u_{AS})}{J^2}$$

$$\tilde{h}_{12}' = \frac{\gamma_1'\beta_B(1-u_{AS})}{J^2}$$

$$\tilde{h}_{13}' = \frac{\gamma_1'\beta_E(1-u_{AS})}{J^2}$$

$$\tilde{h}_{21}' = \frac{\gamma_2'\beta_A(1-u_{BS})}{J^2}$$

$$\tilde{h}_{22}' = -1 - \frac{\tilde{m}(1-u_{BS})}{u_{BS}} + \frac{\gamma_2'\beta_B(1-u_{BS})}{J^2}$$

$$h_{23} = \frac{\gamma_2'\beta_E(1-u_{BS})}{J^2}$$

$$\tilde{h}_{31}' = \frac{\gamma_3'\beta_A(1-u_{ES})}{J^2}$$

$$\tilde{h}_{32}' = \frac{\gamma_3'\beta_B(1-u_{ES})}{J^2}$$

$$\tilde{h}_{33}' = -1 - \frac{\tilde{\ell}(1-u_{ES})}{u_{ES}} + \frac{\gamma_3'\beta_E(1-u_{ES})}{J^2}$$

where $J = 1 + \beta_A(1-u_{AS}) + \beta_B(1-u_{BS}) + \beta_E(1-u_{ES})$.

TABLE CAPTION

Table 1: Newton diagrams* and Newton numbers ν for Application 1.

Footnote to Table 1:

* Only the supports of the Newton frontier are given.

Table 1

	Coefficients of Supports	h_1	h_2	$h_1 h_2$	Degeneracy Condition ($\mu > \nu$)
	$\nu = 1$	ψ_2			
A	$h_{11}, h_{12}, h_{21}, h_{22} \neq 0$				$h_{11}h_{22} - h_{12}h_{21} = 0$
B	$h_{22} = 0,\ h_{11}, h_{21}, h_{12} \neq 0$				
C	$h_{21} = 0,\ h_{11}, h_{12}, h_{22} \neq 0$				
D	$h_{12} = 0;\ h_{11}, h_{21}, h_{22} \neq 0$				
E	$h_{11} = 0,\ h_{12}, h_{21}, h_{22} \neq 0$				
F	$h_{11} = h_{22} = 0,\ h_{12}, h_{21} \neq 0$				
G	$h_{12} = h_{21} = 0,\ h_{11}, h_{22} \neq 0$				
	$\nu = 2$				$4h_{23}h_{24} - h_{25}^2 = 0$
M	$h_{22} = h_{21} = 0,\ h_{11}, h_{12} \neq 0$				or $h_{25}(h_{11}h_{12}h_{25} + h_{12}^2 h_{23} + h_{11}^2 h_{24}) = 0$
I	$h_{12} = h_{22} = 0;\ h_{11}, h_{21} = 0$				$h_{11}h_{24} - h_{14}h_{21} = 0$

Table 1 (continued)

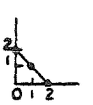
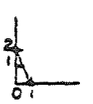
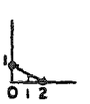
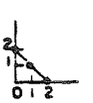
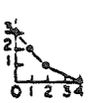
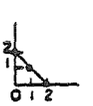
J	$h_{11} = h_{21} = 0,\ h_{21}, h_{22} \neq 0$				$h_{13}h_{22} - h_{12}h_{23} = 0$
K	$h_{11} = h_{12} = 0,\ h_{21}, h_{22} \neq 0$				$h_{13}^2 - 4h_{13}h_{14} = 0$ or $h_{13}(h_{14}h_{21}^2 + h_{13}h_{22}^2 - h_{13}h_{21}h_{22}) = 0$
L	$h_{11} = h_{12} = h_{21} = 0,\ h_{22} \neq 0$				$h_{13}^2 - 4h_{14}h_{13} = 0$
M	$h_{11} = h_{12} = h_{22} = 0,\ h_{21} \neq 0$				$h_{13}^2 - h_{13}h_{14} = 0$
N	$h_{11} = h_{21} = h_{22} = 0,\ h_{12} \neq 0$				$h_{23}^2 - 4h_{23}h_{24} = 0$
O	$h_{12} = h_{21} = h_{22} = 0,\ h_{11} \neq 0$				$h_{23}^2 - 4h_{23}h_{24} = 0$
P	$\nu = 4$ $h_{11} = h_{12} = h_{21} = h_{22} = 0$				$h_{23}^2 - 4h_{23}h_{24} = 0$ or $h_{13}^2 - 4h_{13}h_{14} = 0$ or $256\,h_{13}h_{14}h_{23}h_{24} \cdot (h_{14}h_{23} + h_{13}h_{24})^4 (h_{14}h_{23} - h_{13}h_{23})^4 = 0$

FIGURE CAPTIONS

Figure 1: Newton diagrams for functions (A) f_1' , (B) f_2' , (C) $f_1'f_2'$ for example of Eqn. (3).

Figure 2: General two-dimensional proper Newton diagram. The shaded area S is the area beneath the Newton polygon.

Figure 3: Two-dimensional improper Newton diagram.

Figure 4: Supports of both functions h_1 and h_2 in Application 1 when all the polynomial coefficients are nonzero.

Figure 5: Application 1: Newton diagrams in the case of two-parameter feedback ($b_1 = 1.7431$, $b_2 = 5.7189$).

Figure 6: Newton diagram for $\tilde{h}_1' \cdot \tilde{h}_2'$ in Application 2 for $\tilde{h}_{11} = \tilde{h}_{22} = 0$.

Figure 7: Three reactions of arbitrary order in Application 2. Newton diagram for (A) $\tilde{h}_i'$, (B) $\tilde{h}_i'\tilde{h}_j'$, (C) $\tilde{h}_i'\tilde{h}_j'\tilde{h}_k'$ ($\tilde{h}_{ij}' \neq 0$; i,j,k = 1,2,3

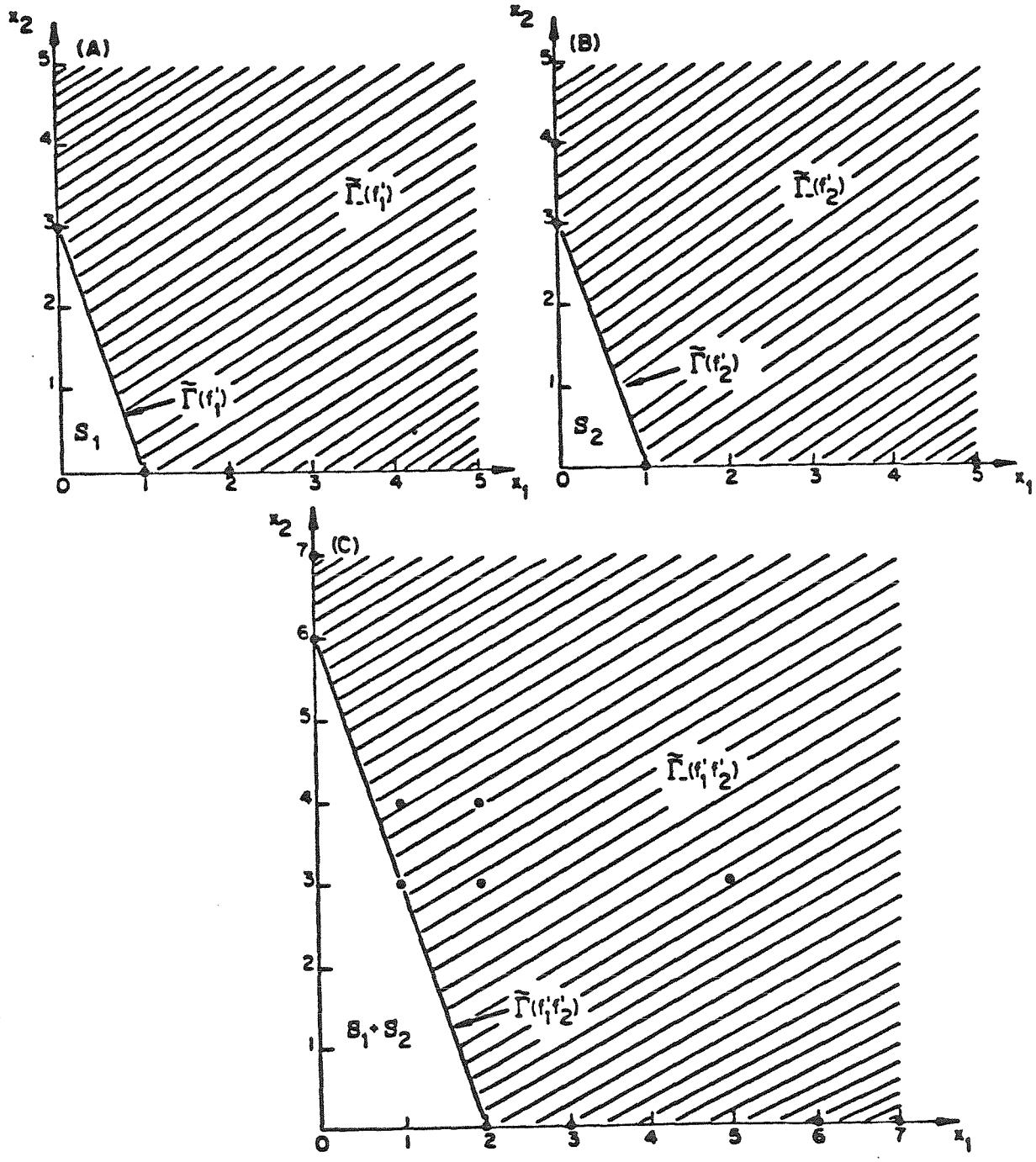

(A)
(B)
(C)
x_2
x_1
$\tilde{\Gamma}_-(f_1')$
$\tilde{\Gamma}(f_1')$
S_1
$\tilde{\Gamma}_-(f_2')$
$\tilde{\Gamma}(f_2')$
S_2
$\tilde{\Gamma}_-(f_1', f_2')$
$\tilde{\Gamma}(f_1', f_2')$
$S_1 + S_2$

FIGURE 1

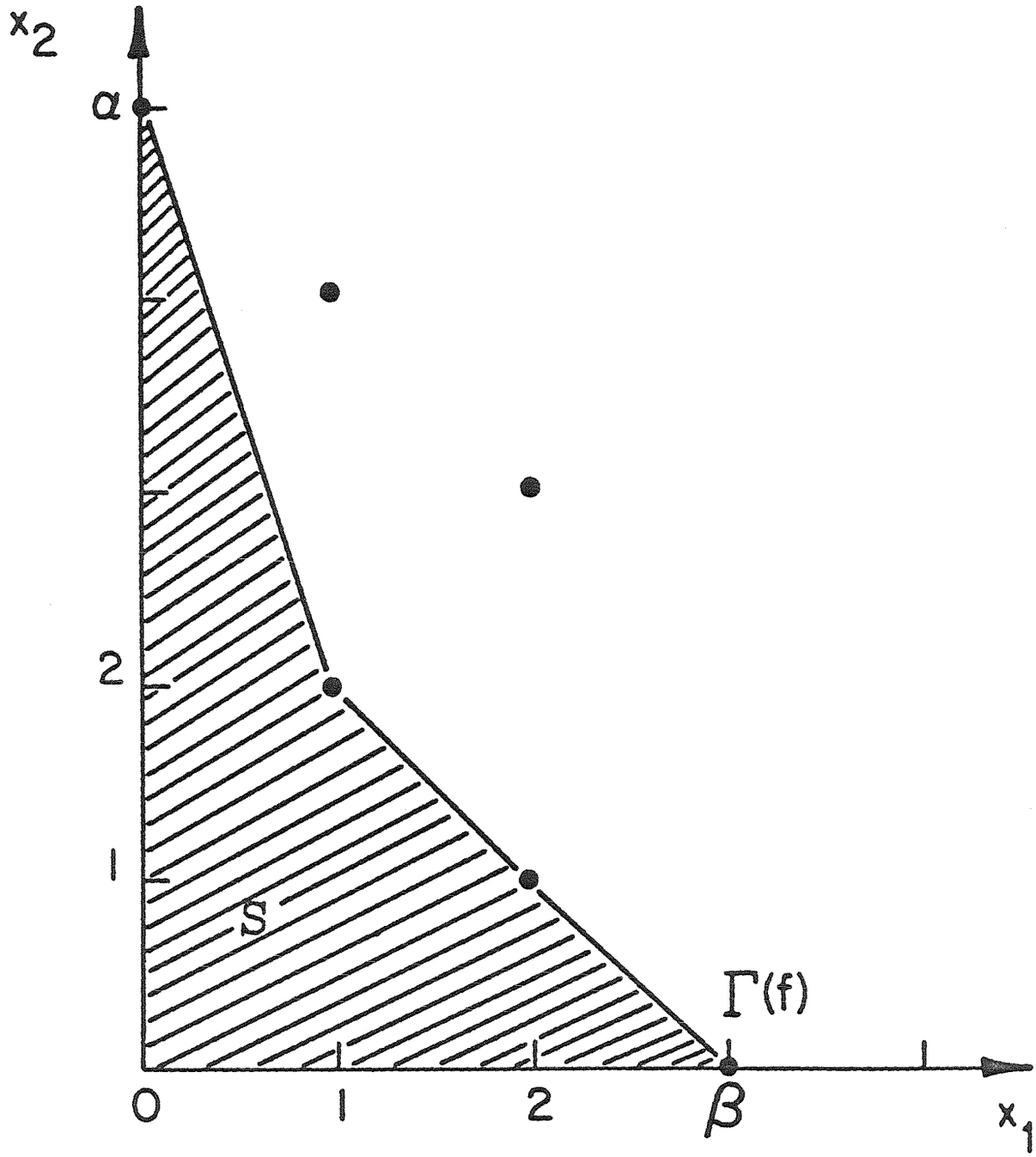


FIGURE 2

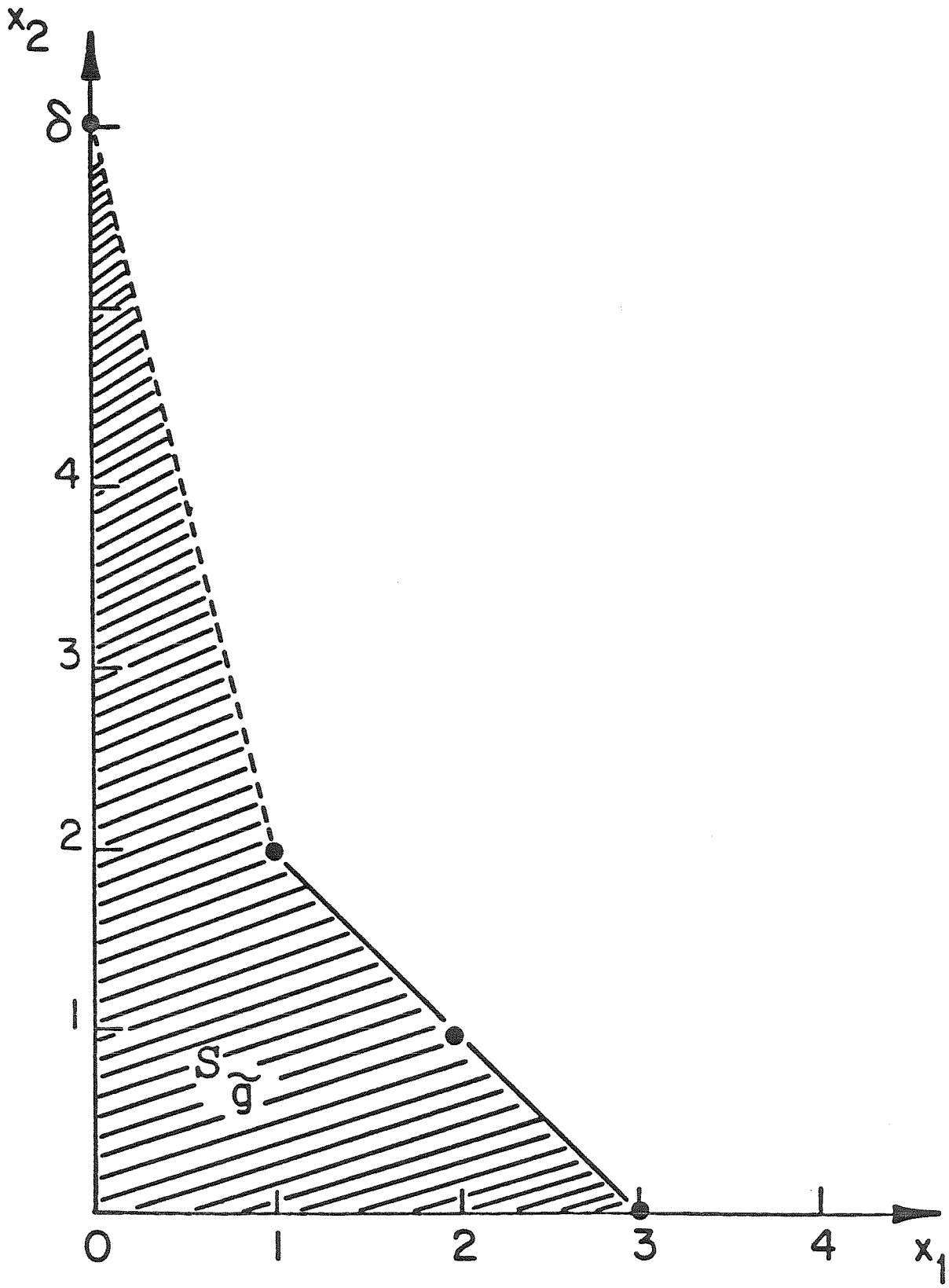


FIGURE 3

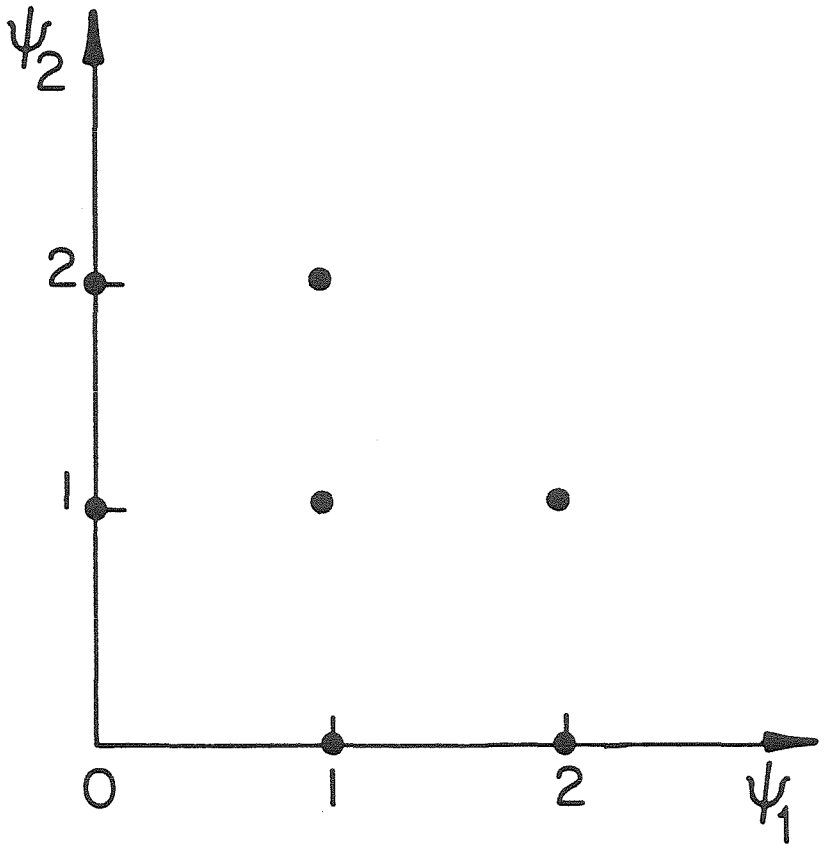


FIGURE 4

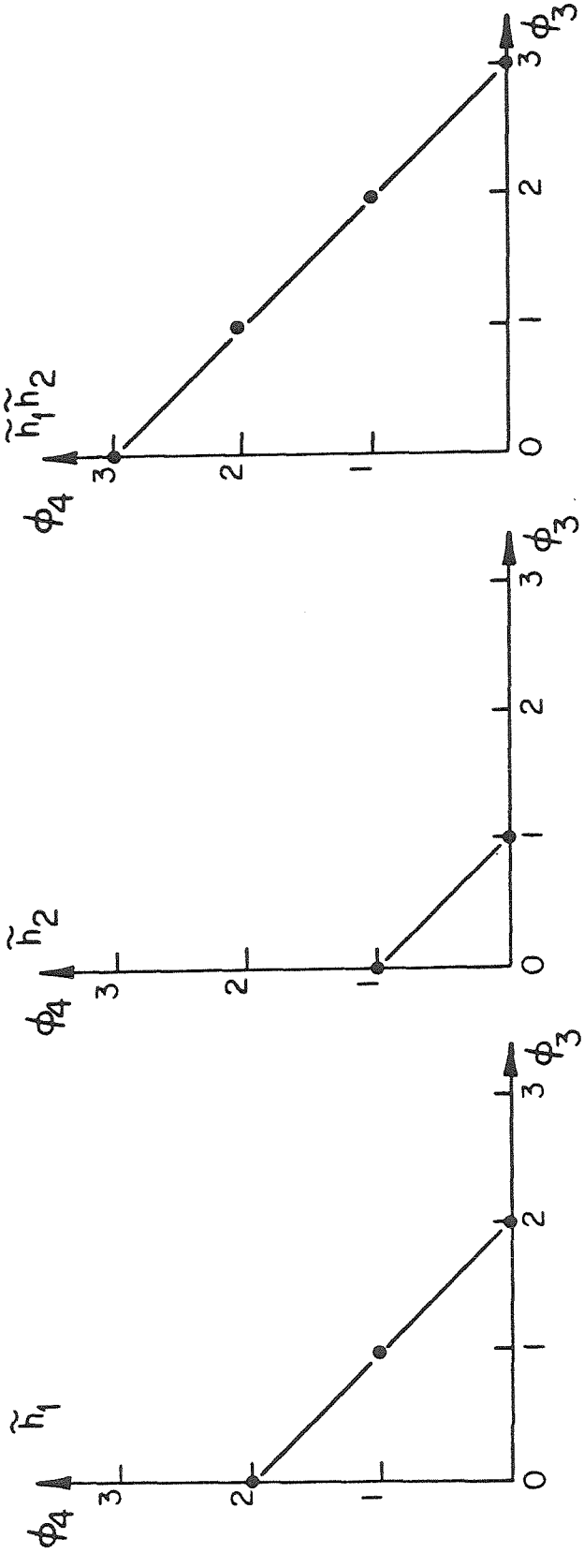

$\tilde{h}_1\tilde{h}_2$
ϕ_4
ϕ_3
$\tilde{h}_2$
ϕ_4
ϕ_3
$\tilde{h}_1$
ϕ_4
ϕ_3
0
1
2
3

FIGURE 5

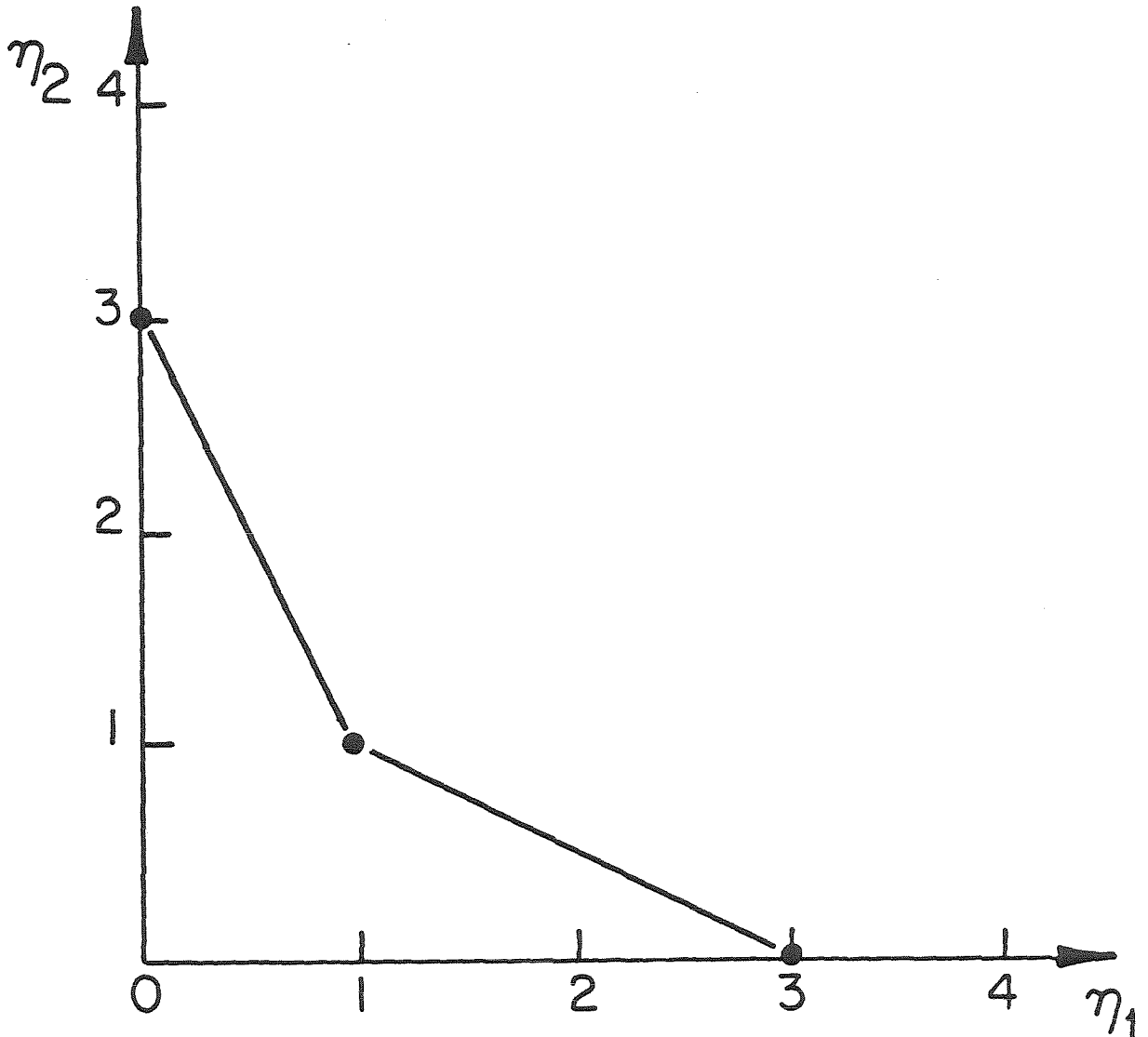
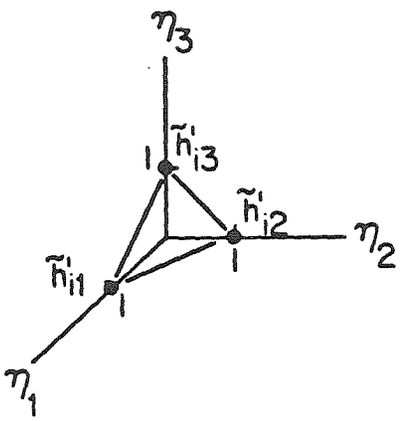
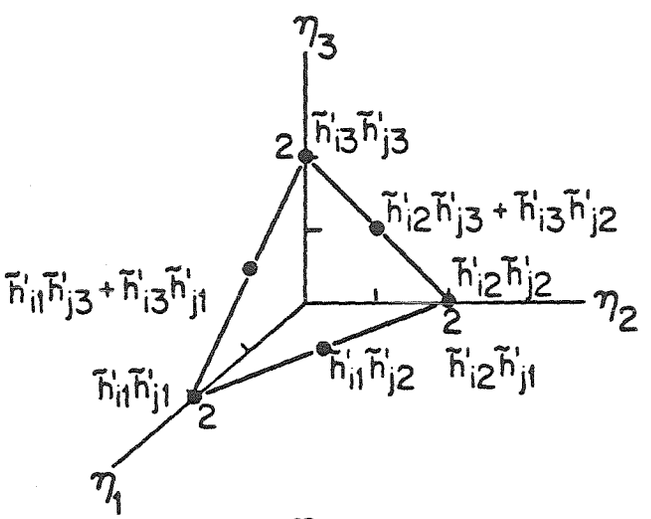


FIGURE 6

(A)


η_3
$\tilde{h}'_{i3}$
1
$\tilde{h}'_{i2}$
η_2
1
$\tilde{h}'_{i1}$
1
η_1

(B)


η_3
2
$\tilde{h}'_{i3}\tilde{h}'_{j3}$
$\tilde{h}'_{i2}\tilde{h}'_{j3} + \tilde{h}'_{i3}\tilde{h}'_{j2}$
$\tilde{h}'_{i1}\tilde{h}'_{j3} + \tilde{h}'_{i3}\tilde{h}'_{j1}$
1
$\tilde{h}'_{i2}\tilde{h}'_{j2}$
η_2
2
$\tilde{h}'_{i1}\tilde{h}'_{j2}$
$\tilde{h}'_{i2}\tilde{h}'_{j1}$
$\tilde{h}'_{i1}\tilde{h}'_{j1}$
2
η_1

(C)

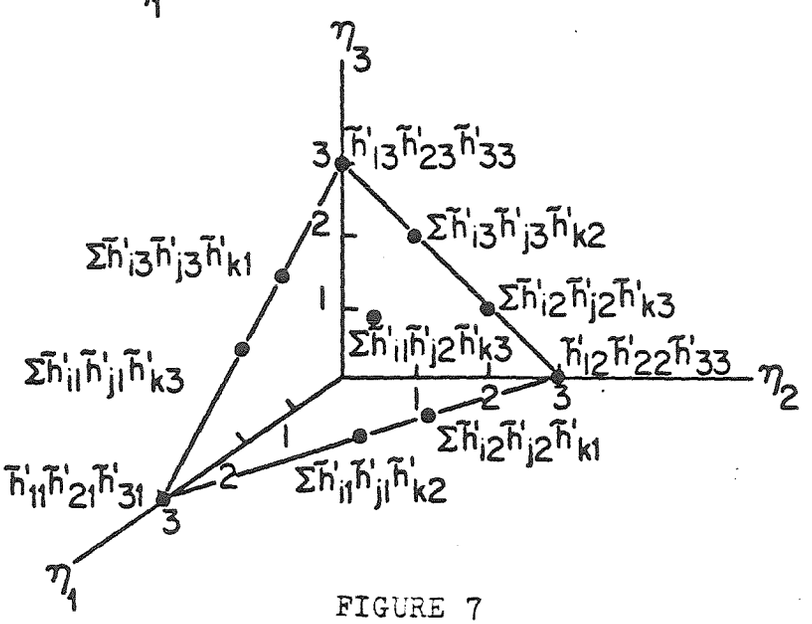

η_3
3
$\tilde{h}'_{i3}\tilde{h}'_{j3}\tilde{h}'_{33}$
2
$\Sigma\tilde{h}'_{i3}\tilde{h}'_{j3}\tilde{h}'_{k2}$
$\Sigma\tilde{h}'_{i3}\tilde{h}'_{j3}\tilde{h}'_{k1}$
1
$\Sigma\tilde{h}'_{i2}\tilde{h}'_{j2}\tilde{h}'_{k3}$
$\Sigma\tilde{h}'_{i1}\tilde{h}'_{j2}\tilde{h}'_{k3}$
$\tilde{h}'_{i2}\tilde{h}'_{22}\tilde{h}'_{33}$
$\Sigma\tilde{h}'_{i1}\tilde{h}'_{j1}\tilde{h}'_{k3}$
1
2
3
η_2
1
$\Sigma\tilde{h}'_{i2}\tilde{h}'_{j2}\tilde{h}'_{k1}$
1
2
$\Sigma\tilde{h}'_{i1}\tilde{h}'_{j1}\tilde{h}'_{k2}$
$\tilde{h}'_{11}\tilde{h}'_{21}\tilde{h}'_{31}$
3
η_1

FIGURE 7

CHAPTER 4 : VERSAL MATRIX FAMILIES, NORMAL FORMS AND HIGHER ORDER BIFURCATIONS IN DYNAMIC CHEMICAL SYSTEMS

INTRODUCTION

Numerous experimental observations of autonomous oscillations in chemical reaction processes [e.g. 1-5] have motivated significant recent interest in the appropriate corresponding mathematical models. Major objectives of research in this connection are the form of kinetic description and the particular parameter values required to obtain a certain type of nonlinear dynamic behavior. It has been suggested that study of this problem may provide useful insight into the underlying mechanism which is manifested by nonlinear oscillations and more complex dynamic phenomena [e.g.1]. Recently, intentional destabilization of steady-state process operation by application of feedback control and observation of the resulting dynamic phenomena has been proposed as a strategy for identifying and evaluating nonlinear process models [6,7]. In this paper classification, realization and local description of nonlinear dynamic behavior near a destabilized steady-state will be considered. The results have important implications for process and control systems analysis and nonlinear dynamic model development and application.

A large class of dynamic chemical process systems can be described by a set of ordinary differential equations of the form

$$\dot{x} = f(x,\nu) \tag{1}$$

where x is a vector of state variables and ν is a vector of system parameters. Despite the large variety of nonlinear models of form (1), it is interesting and important to note that their observable behavior is limited and can be categorized into a few different groups. Examples of different observed characteristics include multiple steady-state behavior [e.g. 2,7-13], existence of stable and unstable periodic oscillations [e.g. 1,7,11,12], relaxation-type oscillations surrounding multiple steady-states [e.g. 7,11,12], complex oscillations [e.g. 14], and chaotic oscillations [e.g. 15,16].

In many circumstances significant understanding of such nonlinear phenomena can be gained by considering the eigenvalue structure of the Jacobian matrix evaluated at some steady-states of System (1) and the dependence of this eigenvalue structure on system parameters. Although study of steady-state eigenvalue structure leads only to conclusions about the local stability properties which derive from linearized model behavior, analysis of the bifurcations that arise as some system parameters are varied can lead to conclusions about the nonlinear structure of the system. At bifurcation, even locally, nonlinear terms cannot be neglected in the process dynamic model. This fact will be explicitly shown in the next section in connection with the theory of normal forms.

Bifurcation implies a change in the local dynamics brought about by variation of parameters. A central concern of this study is the number of parameters which must be varied in order to obtain different types of bifurcations. Subsequently, it is important to investigate stratification of the parameter space with respect to eigenvalue structure [7]. Knowledge of the bifurcation boundaries defines parameter sets for which the qualitative structure of the system dynamics is locally unchanged.

One can use these mathematical tools for two purposes. The first is to understand the sensitivity of different dynamic phenomena to the physical parameters and functional forms used in the model. This is using bifurcation theory as an analytic tool. The second is to design experiments to achieve bifurcation for the purpose of dynamic model development [7]. This is using bifurcation theory as a constructive tool.

In the next section it is seen how a system model can be transformed into a local normal form when the system is close to bifurcation. This provides insight to the question of the minimum dimensionality of a nonlinear model which is necessary to describe adequately the local nonlinear system dynamics. The procedure for obtaining the normal form of a dynamic system is outlined together with the difficulties and advantages of the method.

Next, the important issue of obtaining and translating a certain eigenvalue structure for the system Jacobian is considered. The characteristic equation of the Jacobian matrix and a different approach based on a general representation of the parametric dependence of the corresponding Jordan form are used to investigate the minimum number of system parameters which must be varied in different cases. The characteristic equation approach is then used in an example of a consecutive-competitive isothermal CSTR system with artificial feedback manipulation of the feed concentration. Finally, the dynamics that arise on coupling two oscillating autocatalytic CSTR's in parallel are considered.

BIFURCATION PHENOMENA

The different bifurcation phenomena that are summarized in Table I are based on the structure of the Jordan form of the Jacobian matrix at a particular reference steady-state of the system. Here, the term bifurcation means the appearance locally of new dynamic features when a steady-state becomes unstable as some Jacobian eigenvalues enter the right-hand plane. As mentioned earlier, one can associate different possible dynamic phenomena with particular Jordan form structures. In the sequel, the current state of knowledge along these grounds will be presented [see 17,18].

Here it is convenient to focus on eigenvalue structure rather than Jordan form structure; the two differ only with respect to the question of geometric multiplicity corresponding to repeated eigenvalues. This is a matter of nontrivial importance. However, since the geometric multiplicity is most often unity, one can assume for the sake of preliminary analysis that a particular eigenvalue structure is usually associated with a corresponding particular Jordan form structure. After identifying bifurcation conditions of interest for a particular system, the corresponding Jordan form structure should be evaluated to verify this assumption.

A D_1 bifurcation occurs when, on varying some parameter, a single real eigenvalue becomes positive. The steady-state becomes unstable and trajectories lead far from it in a monotonic fashion. This bifurcation phenomenon also may involve (and usually it will) steady-state bifurcation. Thus, as the steady state becomes unstable, other steady states usually appear, and exchange of stability occurs. Typically, trajectories lead to one of the new stable steady states. Exchange of stability under such conditions is implied by index theory [19].

A D_2 bifurcation occurs when a complex conjugate pair of Jacobian eigenvalues crosses the imaginary axis as some parameter is changed. The steady state becomes unstable, and periodic solutions, which may be stable or unstable, appear. In the former case, trajectories lead to nearly harmonic periodic solutions which are the only stable structures in the neighborhood of the reference steady state. This is the classical case of supercritical Hopf bifurcation. It is also possible that on varying the parameters the structure changes from a stable steady state surrounded by an unstable limit cycle to an unstable steady state. This is the less common case of subcritical Hopf bifurcation.

Next, in the hierarchy of bifurcation categories (often called *strata*) is the case of F_1 bifurcation. Close to an F_1 bifurcation point one can expect steady-state multiplicity and periodic solutions of the relaxation type as well as of harmonic form. Depending on the initial state near the reference steady state, trajectories can lead to different steady states or to a limit cycle [7,17,20]. Notice that D_1 bifurcation can be observed by a model of any dimensionality. D_2 and F_1 bifurcations, however, require at least a two-dimensional model.

F_2 bifurcation involves three eigenvalues crossing the imaginary axis. In addition to the previous dynamic phenomena, one can anticipate that, close to an F_2 bifurcation, toroidal oscillations may occur. F_2 bifurcation usually also involves steady-state bifur-

cation. Such systems have been studied by Ruelle and Takens [21], Langford [22] and others [see also 23].

F_3 bifurcation involving two conjugate imaginary pairs of Jacobian eigenvalues can produce complicated multipeak oscillations. F_3 bifurcation does not involve steady-state bifurcation. Finally, with G_1 bifurcation, depending on the type of manifold [24], it is possible that chaotic oscillations arise.

It must be emphasized that the local dynamic features mentioned above in connection with different eigenvalue structures at bifurcation are the most complex that are expected; simpler behavior is also possible. For example, a system exhibiting F_1 bifurcation may exhibit relaxation oscillations, harmonic oscillations, or escape from the reference steady-state neighborhood near bifurcation. A G_1 bifurcation may produce anything ranging from chaos to escape from the steady-state. Thus, a higher order bifurcation increases the possibilities of local dynamic phenomena, but it does not guarantee any particular type of dynamic phenomena. The Venn diagram in Figure 1 summarizes this point and the possible dynamic features near each bifurcation stratum in pictorial form.

Consequently, in order to obtain toroidal or chaotic oscillations in the neighborhood of the reference steady-state, the model dimensionality must be at least three. The same conclusion also follows from the fact that trajectories in the phase plane for a two-dimensional system cannot intersect except at singular points [e.g. 26].

The summary above shows how one can associate different possible local dynamic behavior with the eigenvalue structure at bifurcation. Since such configurations can be obtained with models of order three or four, it is clear that all different qualitative characteristics like multiplicity of steady-state and different types of oscillations can be produced by models of low dimensionality. Higher dimensionality is responsible for fine tuning of system behavior which may not be observable due to measurement limi-

tations and noise. The theory of normal forms very nicely explains why a model of high dimensionality has an observable behavior similar to that of a low-dimensional model, with only a few of the system modes playing an important role. The basic theory of normal forms is outlined in the next section.

It should be emphasized that the conditions presented here for appearance of different dynamic features refer only to local phenomena —in the state space near the reference steady state and in the parameter space near the values of bifurcation. Complex nonlinear features can also arise in other ways such as bifurcation from a limit cycle leading to period doubling and eventually chaotic oscillations.

NORMAL FORMS

Given a system of the form (1), there is always a smooth transformation of variables such that all trajectories close to a steady state are transformed to those of a simpler system. The simplest form of a system that retains all characteristic (topological) nonlinear local features of the original system (1) is called the normal form of the system (1) [17,26]. The normal form is generally a lower order nonlinear system such as

$$\dot{\mathbf{y}} = \mathbf{g}(\mathbf{y}) \tag{2}$$

where $\mathbf{y}(t) \in E^m$ and $m \leq n$. The function $\mathbf{g}(\mathbf{y})$ typically has a simpler (polynomial) form than the function $\mathbf{f}(\mathbf{x})$. The price that one pays for such a simplification is usually a complicated nonlinear transformation of the form

$$\mathbf{y} = \varphi(\mathbf{x}) \tag{3}$$

from the original state variables $\mathbf{x}$ to the "artificial" state variables $\mathbf{y}$ of the new system in normal form. The parameters of the new system are in general nonlinear combinations of the original system parameters.

Suppose that the eigenvalues λ_i of the Jacobian matrix J of system (1) are divided into two sets, $K' = \{\lambda_i | Re(\lambda_i) = 0\}$, and $K'' = \{\lambda_i | Re(\lambda_i) \neq 0\}$. Denote by m the number of eigenvalues with zero real parts; i.e., the number of members of the set K'. Then there exists a linear transformation of system (1) such that the Jacobian J of the new system has the structure:

$$J = \begin{bmatrix} B & O \\ C & D \end{bmatrix} \tag{4}$$

where B is an m×m Jordan canonical matrix with eigenvalues $\lambda_1,\ldots\lambda_m \in K'$, D is an (n - m)×(n - m) matrix with eigenvalues $\lambda_{m+1},\ldots\lambda_n \in K''$, O is an m×(n - m) zero matrix and C is an (n - m)×m matrix. Then, system (1) becomes

$$\dot{x}' = Bx' + X'(x',x'') \tag{5.1}$$

$$\dot{x}'' = Cx' + Dx'' + X''(x',x'') \tag{5.2}$$

If the set K'' of eigenvalues is nonresonant,[a] the last system by formal change of variables

$$x' = y' + h'(y') \tag{6.1}$$

$$x'' = y'' + h''(y') \tag{6.2}$$

can be reduced to the normal form on an invariant m-dimensional surface [26]

$$\dot{y}' = By' + Y'(y',0)\,, \tag{7}$$

the invariant surface being given by $y'' = 0$.

If the set of all system eigenvalues is nonresonant (which requires that the system is not at bifurcation), the original system may be transformed by Eqn. (6) to a linear system. If the set of system eigenvalues is resonant but the system is not at bifurcation,

[a] The p-tuple $\varepsilon = (\varepsilon_1,\varepsilon_2,\ldots\varepsilon_p)$ of eigenvalues is said to be resonant if a relationship of the following form exists among these eigenvalues [26]. $\varepsilon_s = (l, \varepsilon)$ Here, ε_s is any eigenvalue in the p-tuple, $l = (l_1,l_2,\ldots l_p)$, all elements of l are non-negative integers and $\sum l_j > 2$. Clearly, bifurcation is a special case of resonance.

transformation (6) does not exist, but the dynamics near the reference steady-state may still be characterized by the linearized model. A certain model can, therefore, be safely linearized when far from bifurcation, and its trajectories behave close to those of the linearized system. Close to bifurcation, however, the validity of the linear approximation is restricted to smaller and smaller radius about the steady-state. Exactly at bifurcation, the system model cannot be linearized, its trajectories being equivalent only to those of a nonlinear model (Eqn. (7), the normal form) even for infinitesimal radius (perturbation). The functions h' and h" in Eqns. (6) are found by solving a so-called homological equation [26,27].

The theory of normal forms provides a formal method of model reduction retaining the essential local nonlinear structure of a dynamic system. It is clear that only the modes of the system close to the imaginary axis are important in determining the nonlinear nature of the system. As a result, by forcing a system to bifurcation, one can find out much about its nonlinear structure.

The major limitation of normal forms is the noninvertibility of transformation (6). Thus, there are many systems of the form (1) that after transformation have the same normal form. This fact limits the use of the theory of normal forms as a constructive tool. However, forcing a given system model to bifurcation and knowing its normal form gives insight to the possible qualitative dynamic characteristics of the system when it is perturbed from the bifurcation point.

ATTAINMENT OF BIFURCATION STRUCTURE USING THE CHARACTERISTIC EQUATION

Any model of the form (1) that has eigenvalues of the steady-state Jacobian on the imaginary axis is structurally unstable. That is, a small change in one or more parameter values changes the eigenvalue configuration, possibly the Jordan form block structure, and the topology of the local dynamics. In a "typical" situation, the Jacobian has

no eigenvalues on the imaginary axis, but study of the effect of parameter perturbations from "atypical", structurally unstable situations provides knowledge of the different structurally stable systems that can arise. The minimum number of parameters that must be varied independently to obtain different structurally unstable forms is considered in what follows using the characteristic equation of the Jacobian at the steady state. As mentioned before, achievement of a particular eigenvalue configuration does not guarantee a particular bifurcation stratum; that depends on realizing a particular structure in the Jordan form of the system Jacobian. Consequently, parametric requirements for obtaining different Jordan block structures are considered in the Appendix. It is shown there that if a particular Jordan block structure can be obtained, the number of parameters required is the same as the number of parameters required to realize the corresponding eigenvalue configuration.

Consider the system (1). This system has a characteristic equation for the Jacobian of the form

$$s^n + \tilde{a}_1 s^{n-1} + \tilde{a}_2 s^{n-2} + \cdots + \tilde{a}_{n-1} s + \tilde{a}_n = 0 . \tag{8}$$

The coefficients $\tilde{a}_i$ of this polynomial of degree n are in general functions of the system parameters ν. Since bifurcations of different types imply vanishing of the real part of one or more eigenvalues, different algebraic conditions involving the $\tilde{a}_i$ may be derived that must be satisfied to obtain a certain eigenvalue structure. These are summarized below.

i. D_1 bifurcation

$$\tilde{a}_n = 0 . \tag{9}$$

One algebraic condition that may be satisfied by varying one system parameter.

ii. D_2 bifurcation (Hopf)

$$(i\omega)^n + \bar{a}_1(i\omega)^{n-1} + \bar{a}_2(i\omega)^{n-2} + \cdots + \bar{a}_{n-1}(i\omega) + \bar{a}_n = 0 . \tag{10}$$

Separating real and imaginary parts, one obtains two equations. Eliminating ω^2, a single equation should be satisfied by the coefficients $\bar{a}_i$. Furthermore since ω^2 must be positive, one obtains in addition an inequality condition. Variation of one parameter can force the equality condition to be satisfied, but this does not guarantee that the inequality will also be satisfied. Thus, in general, one needs to consider variation of (at least) two parameters. It is presumed here that the system parameters varied influence the two conditions involved such that the conditions can be satisfied for some admissible parameter values. This will not necessarily be true for any two system parameters. More than two system parameters may be required, and it may happen, if the system does not possess appropriate structure, that no choice of parameters may satisfy the requisite conditions. Thus the number of parameters mentioned here is in some sense (see Discussion) a minimum value. Similar comments apply to all other cases in this list.

iii. F_1 bifurcation

$$\bar{a}_n = \bar{a}_{n-1} = 0 . \tag{11}$$

Two parameters are needed to satisfy these equations.

iv. F_2 bifurcation

$$\bar{a}_n = 0 \tag{12.1}$$

$$(i\omega)^{n-1} + \bar{a}_1(i\omega)^{n-2} + \cdots + \bar{a}_{n-1} = 0 . \tag{12.2}$$

As in the Hopf case, elimination of ω^2 between the two equations which result from separation of real and imaginary parts of Eqn. (12.2) gives eventually two equalities and a single inequality, implying that, in general, it may take three parameters to satisfy the required conditions.

v. F_3 bifurcation

In this case it is easy to see that two equalities and two inequalities should be satisfied which would require two to four parameters.

vi. G_1 bifurcation

$$\tilde{a}_n = \tilde{a}_{n-1} = \tilde{a}_{n-2} = 0 . \tag{13}$$

At least three parameters must be adjusted to satisfy these three equations.

It is not difficult to show that the number of parameters required to move a given eigenvalue configuration from zero real part to real part equal to $+\varepsilon$ is the same as the number of parameters used to obtain the original arrangement on the imaginary axis. Thus, the parameter numbers determined above to obtain a certain eigenvalue configuration at bifurcation are the same number of parameters needed to stabilize that eigenvalue structure and to translate it into the right-half plane.

EXAMPLE I: FEEDBACK PARAMETERS NEEDED TO BRING A CONSECUTIVE-COMPETITIVE REACTION SYSTEM IN A CSTR TO BIFURCATION

To illustrate how the different bifurcation conditions can be satisfied by variation of parameters, consider the following reaction sequence taking place in a CSTR:

$$\tilde{B} + \tilde{A} \xrightarrow{\tilde{k}_1} \tilde{C} + \tilde{Z}$$

$$\tilde{C} + \tilde{A} \xrightarrow{\tilde{k}_2} \tilde{D} + \tilde{Z} \tag{14}$$

Assuming mass action kinetics, the transient species balances become

$$\frac{d[\tilde{A}]}{dt} = -\tilde{k}_1[\tilde{B}][\tilde{A}] - \tilde{k}_2[\tilde{C}][\tilde{A}] - \frac{1}{\tau}([\tilde{A}] - [\tilde{A}]^0)$$

$$\frac{d[\tilde{B}]}{dt} = -\tilde{k}_1[\tilde{B}][\tilde{A}] - \frac{1}{\tau}([\tilde{B}] - [\tilde{B}]^0)$$

$$\frac{d[\tilde{C}]}{dt} = \tilde{k}_1[\tilde{B}][\tilde{A}] - \tilde{k}_2[\tilde{C}][\tilde{A}] - \frac{1}{\tau}[\tilde{C}] . \tag{15}$$

Introducing dimensionless quantities (see Nomenclature), Eqns. (15) become

$$\frac{d\tilde{x}}{dt} = -\alpha_1\tilde{x}\tilde{y} - \alpha_2\tilde{x}\tilde{z} - (\tilde{x} - u_A)$$

$$\frac{d\tilde{y}}{dt} = -\alpha_1\tilde{x}\tilde{y} - (\tilde{y} - u_B)$$

$$\frac{d\tilde{z}}{dt} = \alpha_1\tilde{x}\tilde{y} - \alpha_2\tilde{x}\tilde{z} - \tilde{z} . \tag{16}$$

The steady state equations are reduced to a single equation in x which is a polynomial of degree three:

$$\alpha_1\alpha_2x^3 + (2\alpha_1\alpha_2u_B + \alpha_1 + \alpha_2 - u_A\alpha_1\alpha_2)x^2 + (1 + \alpha_1u_B - \alpha_1u_A - \alpha_2u_A) = 0 . \tag{17}$$

For $u_B = \alpha_1 = \alpha_2 = 1$, the steady-state for $u_A = 1$ is easily seen to be unique, and it is:

$$\tilde{x}_s = 0.532089, \quad \tilde{y}_s = 0.652704, \quad \tilde{z}_s = 0.226682 \tag{18}$$

with eigenvalues

$$-1.971782 \pm 10.392386 \text{ and } -1.000000 . \tag{19}$$

Now consider introduction of feedback in which the feed concentration of A is varied according to

$$u_A = 1 - b_1(x - 0.532089) - b_2(y - 0.652704) - b_3(z - 0.226682) . \tag{20}$$

The characteristic equation of the Jacobian evaluated at the reference steady-state is:

$$s^3 + (4.9256 + b_1)s^2 + (7.9262 + 3.0462b_1 - 0.6527b_2 + 0.4260b_3)s$$

$$+ (4.0006 + 2.3198b_1 - 0.9941b_2 + 0.3074b_3) = 0 . \tag{21}$$

The question then is what are the conditions for the different bifurcation phenomena. Since the dimensionality of the system is three, the only possible bifurcation

phenomena are: D_1, D_2, F_1, F_2 and G_1. Let

$$C_1 = 4.9256 + b_1$$

$$C_2 = 7.9262 + 3.0462b_1 - 0.6527b_2 + 0.4260b_3$$

$$C_3 = 4.0006 + 2.3198b_1 - 0.9941b_2 + 0.3074b_3 \tag{22}$$

Then Eqn. (21) reads

$$s^3 + C_1 s^2 + C_2 s + C_3 = 0\,, \tag{23}$$

and Eqns. (9-13) in this case become:

i. D_1 bifurcation:

$$C_3 = 0 \tag{24}$$

ii. D_2 bifurcation (Hopf):

$$\left.\begin{array}{l} C_3 - C_1 C_2 = 0 \\ C_2 > 0 \end{array}\right\} \tag{25}$$

iii. F_1 bifurcation:

$$C_2 = C_3 = 0 \tag{26}$$

iv. F_2 bifurcation:

$$\left.\begin{array}{l} C_3 = 0 \\ C_1 = 0 \\ C_2 > 0 \end{array}\right\} \tag{27}$$

v. G_1 bifurcation:

$$C_1 = C_2 = C_3 = 0\,. \tag{28}$$

Substituting Eqn. (22) into the above conditions shows how feedback gain values must be adjusted to obtain different types of bifurcation for the closed-loop system. Conducting this analysis shows that, with manipulation of only one feedback parame-

ter, only D_1 bifurcation is observed for this system. With two feedback parameters available, D_1, D_2 and F_1 are observed. The decrement diagram [7] for this case is shown in Figure 2. For other systems in which the inequality constraints mentioned above for D_2 and F_2 bifurcation are satisfied, it may be possible to obtain D_2 and F_2 bifurcations by varying one- and two-system parameters, respectively. The present example does not possess these properties. With three feedbacks, all of D_1, D_2 (Hopf), F_1, F_2 and G_1 may be obtained for this system. Higher order bifurcations cannot be obtained regardless of the number of feedback parameters because of the system dimensionality. As mentioned earlier, the bifurcations obtained in closed-loop operation are expected to provide sensitive information on the local nonlinear properties of the reactor.

EXAMPLE II: AUTOCATALYTIC REACTION IN COUPLED CSTRs

Consider the autocatalytic reaction

$$\hat{A} \rightarrow \hat{B} \tag{29.1}$$

$$\hat{B} \rightarrow \hat{C} \tag{29.2}$$

taking place in two isothermal stirred tank reactors coupled in parallel. The coupling may be effected by a membrane separating the two reactors which allows all species to diffuse from one reactor to the other or as an external feedback control. Kumar et al. [28] assumed an exponential dependence of the rate of reaction (29.1) on the concentration of $\hat{B}$. They found that if the reactors are both in an oscillating regime but at different operating conditions, the behavior of the system depends on the coupling constant. For large values of the coupling parameter, the reactors synchronize, whereas for small values of the coupling constant, each reactor oscillates with a different frequency giving rise to a combined output of complicated waveform. They found that the interaction caused no effect on the qualitative waveform of the concentration oscillations in each individual reactor. The stiffness of the system model with the assumed exponential nonlinearity did not allow for a thorough parametric study of

possible dynamic behavior. Gray and Scott [29] assumed different mass action kinetics to describe the autocatalytic reaction and found that if the reaction is assumed to proceed according to

$$\hat{A} + 2\hat{B} \xrightarrow{k_1} 3\hat{B}$$

$$\hat{B} \xrightarrow{k_2} \hat{C} \,. \tag{30}$$

oscillations occur in a single CSTR for some parameter values. The dynamics of a coupled isothermal reactor system in which reactions (30) occur are analyzed next.

The dynamic system is described by the following material balances

$$\frac{d[\hat{A}]_I}{dt} = -\hat{k}_1[\hat{A}]_I[\hat{B}]_I^2 + \frac{[\hat{A}]_I^0 - [\hat{A}]_I}{\hat{t}_R} + \hat{d}_1([\hat{A}]_{II} - [\hat{A}]_I) \tag{31.1}$$

$$\frac{d[\hat{B}]_I}{dt} = \hat{k}_1[\hat{A}]_I[\hat{B}]_I^2 + \frac{[\hat{B}]_I^0 - [\hat{B}]_I}{\hat{t}_R} - \hat{k}_2[\hat{B}]_I + \hat{d}_2([\hat{B}]_{II} - [\hat{B}]_I) \tag{31.2}$$

$$\frac{d[\hat{A}]_{II}}{dt} = -\hat{k}_1'[\hat{A}]_{II}[\hat{B}]_{II}^2 + \frac{[\hat{A}]_{II}^0 - [\hat{A}]_{II}}{\hat{t}_R} + \hat{d}_1([\hat{A}]_I - [\hat{A}]_{II}) \tag{31.3}$$

$$\frac{d[\hat{B}]_{II}}{dt} = \hat{k}_1'[\hat{A}]_{II}[\hat{B}]_{II}^2 + \frac{[\hat{B}]_{II}^0 - [\hat{B}]_{II}}{\hat{t}_R} - \hat{k}_2'[\hat{B}]_{II} + \hat{d}_2([\hat{B}]_I - [\hat{B}]_{II}) \,. \tag{31.4}$$

Assuming $[\hat{A}]_I^0 = [\hat{A}]_{II}^0$ and $[\hat{B}]_I^0 = [\hat{B}]_{II}^0$ and introducing dimensionless variables (see Nomenclature), one obtains

$$\frac{d\hat{x}}{dt} = -\hat{a}_1\hat{x}\hat{y}^2 + 1 - \hat{x} + \hat{t}_1(\hat{x}' - \hat{x}) \tag{32.1}$$

$$\frac{d\hat{y}}{dt} = \hat{a}_1\hat{\varepsilon}\hat{x}\hat{y}^2 - \hat{a}_2\hat{\varepsilon}\hat{y} + 1 - \hat{y} + \hat{t}_2(\hat{y}' - \hat{y}) \tag{32.2}$$

$$\frac{d\hat{x}'}{dt} = -\hat{\varepsilon}_1\hat{x}'\hat{y}'^2 + 1 - \hat{x}' + \hat{t}_1(\hat{x} - \hat{x}') \tag{32.3}$$

$$\frac{d\hat{y}'}{dt} = \hat{\varepsilon}_1\hat{\varepsilon}\hat{x}'\hat{y}'^2 - \hat{\varepsilon}_2\hat{\varepsilon}\hat{y}'\hat{y} + 1 - \hat{y}' + \hat{t}_2(\hat{y} - \hat{y}') \,. \tag{32.4}$$

Simulations were performed for $\alpha_1 = 1.2$, $\alpha_2 = 0.45$, $\beta_1 = 1.0$, $\beta_2 = 0.375$ and $g = 15$ parameter values for which each reactor oscillates at different frequencies. The rate constants for reactor 1 are larger than those in reactor 2, a situation which might be realized by operating reactor 1 at higher temperature.

Varying the coupling constants f_1 and f_2, different behavior was found. Referring to the $f_1 - f_2$ parameter space illustrated in Figure 3, four distinct regions exist. In regions I and II, there is a single unstable steady state for the coupled reactor system. In regions III and IV there are three steady states. The two additional ones arise from a limit point bifurcation which occurs along the line (a). One is unstable and the other is stable, such that all trajectories for f_1 and f_2 in regions III and IV lead to the single stable steady state. This steady-state corresponds to high $\hat{B}$ concentrations in the "cooler" reactor (reactor 2) and low $\hat{B}$ concentrations in the "warmer" reactor (reactor 1). One can easily see the practical significance of this result. Coupling two oscillating reactors, stable steady-state behavior is obtained for some range of values of the coupling gains; the oscillations have been quenched.

The line that separates regions I and III from regions II and IV represents the locus along which the eigenvalue structure for the unstable steady state changes from that of two complex conjugate pairs with positive real part to that of a single complex pair with positive real part as a pair of eigenvalues crosses the imaginary axis along line (b). This explains why for large values of f_1 and f_2 the two reactors synchronize. When f_1 and f_2 are in region II, the coupled reactor system oscillates with a frequency near the imaginary part of the single complex conjugate pair with positive real part.

In region I, oscillations of interesting form arise as the system now has two basic frequencies influencing its dynamics. In Figures 4-6, the form of oscillations for three sets of values of f_1 and f_2 in region I are shown. The steady-state values and eigenvalues for each of these parameter sets are shown on Table II. For $(f_1, f_2) = (0.01, 0.01)$

(Figure 4) the "hot" reactor oscillations are single-peak regular oscillations while the "cool" reactor oscillations are of different frequency, multipeak and of different form. There is a period of about 12.2 time units evident. For $(f_1,f_2) = (0.01,0.1)$ (Figure 5), the oscillations of both reactors are modulated, but again the effect is more dramatic for the "cool" reactor. For $(f_1,f_2) = (0.1,0.01)$ (Figure 6), the "hot" reactor is again only slightly modulated with a dramatic influence in the form of oscillations of the "cool" reactor.

The eigenvalue structure of the steady state in region I suggests that the system may be viewed as resulting from an F_2 bifurcation. Fixing $(f_1,f_2) = (0.01,0.1)$ and varying only two parameters, α_1 and β_1, the steady state changes as well as its eigenvalue structure. An F_2 bifurcation point is found at $(\alpha_1 = 1.7489, \beta_1 = 1.1341)$. The steady state at these values is

$$\bar{x}_s = 0.154, \quad \bar{y}_s = 1.769, \quad \bar{z}_s = 0.180, \quad \bar{w}_s = 2.003 .$$

with eigenvalues:

$$\lambda_{1,2} = \pm 6.0323111, \quad \lambda_{3,4} = \pm 5.000145i .$$

For larger values of α_1 and β_1, the reference steady state is stable. The F_2 bifurcational structure was achieved here by varying only two parameters because the system already had the necessary underlying structure. Other systems may require up to four parameters to obtain an F_2 bifurcation.

CONCLUSIONS AND DISCUSSION

It has been seen how a certain dynamic system can be brought to bifurcation by introducing feedback. The theory of normal forms provides insight into why a system at bifurcation manifests distinctive nonlinear features. This supports previously proposed strategies for system model identification and validation based on experiments near bifurcation conditions. Also, normal form theory allied with bifurcation theory

shows that low-order models suffice in general to describe a broad class of nonlinear phenomena. Bringing a system to its normal form involves a complicated transformation, which makes this procedure not very tractable in general. Furthermore, since this transformation is not invertible, it is impossible to use the normal form of a system as a constructive engineering tool, for example, to establish a control law or perform an optimization.

However, transforming a given model to normal form, or simply studying the general normal form corresponding to the bifurcation Jordan block structure of a given model, provides a convenient, locally topologically equivalent, low-order nonlinear model which can be used to explore possible dynamic phenomena of the original model. This approach will be illustrated in future papers on feedback control loops in enzyme-catalyzed reaction sequences and periodically forced chemical reactors.

In the above discussion, the number of parameters in the characteristic equation which must be adjusted to achieve different eigenvalue configurations was addressed; the Appendix gives a similar analysis based on manipulation of entries in the Jordan form of the system Jacobian at the reference steady state. As noted earlier, the number of parameters involved for each bifurcation stratum is the same from either the characteristic equation or the Jordan block perspective. There are, however, several subtleties which should be mentioned now concerning the question of the required number of parameters.

First, consider the case where one of the required constraints is an inequality constraint. This implies that it is satisfactory, from the point of view of obtaining a given eigenvalue or Jordan block structure, that a certain parameter simply be positive or negative. This is not an especially demanding condition and it may be met for many systems. Then the inequality constraint is not active, and one can obtain the desired eigenvalue configuration without regard to the inequality constraint and with conse-

quently one fewer manipulated parameter. For example, the D_2 (or Hopf) bifurcation case in general requires two parameters. However, since one of the constraints involved is an inequality, Hopf bifurcations have been observed on varying a single parameter for many reactor models. This analysis shows that in some cases, by varying a second parameter, a system which does not exhibit a D_2 bifurcation with one parameter can be made to Hopf bifurcate. This was the case for the first example discussed above. The second example, on the other hand, shows a case where, the two inequality constraints being automatically satisfied, variation of only two parameters suffices to obtain an F_3 bifurcation.

Types of bifurcation of higher order than D_2 usually require precise manipulation of more than one parameter. Achieving an F_1 bifurcation requires that two parameters be adjusted to precise values to satisfy two equality constraints. This means that dynamic behavior characteristic of an F_1 bifurcation will generally not be observed upon varying a single parameter. To find such behavior with one parameter varying requires substantial luck. To see that it is possible, however, consider two parameters p_1 and p_2 and suppose that the values of these parameters which give the F_1 eigenvalue configuration are p_1° and p_2°. If by chance the value of the parameter p_2 is chosen near the value of p_2° and p_1 is varied, when p_1 is near p_1°, eigenvalue configurations near the F_1 configuration will arise. The accompanying dynamic behavior may resemble that for an F_1 bifurcation. However, variation of p_1 above will not necessarily produce all possible different dynamic behaviors typical of an F_1 bifurcation (Figure 1).

Another point that should be made is that although the distinctions between different kinds of bifurcations described above are presented as sharp and clear, this is often not the case in practice. When some of the Jacobian eigenvalues are found in the right-half plane, their predecessors are not uniquely defined. Depending on the parameters that one allows to vary, one may find that arriving at this eigenvalue structure may be viewed as the consequence of different types of bifurcations.

Although this detracts in some degree from the practical utility of the bifurcation theory discussed above in analyzing nonlinear system dynamics, it does not render the above conclusions useless or trivial. While developing mathematical models for chemical reaction networks and chemical reactors which exhibit oscillations has become increasingly successful, the same cannot be said for models which generate more complicated kinds of nonlinear oscillations. The discussion above explains in part why finding more complex oscillations from the model is more difficult than finding a simple Hopf bifurcation.

The framework summarized also provides guidance on how to identify candidates for models and corresponding parameters which do, possibly, give different types of complex dynamics. To obtain the apparently irregular types of oscillations characteristic of motion on a torus, one should look for the F_2 Jordan block structure, or, more practically, the corresponding eigenvalue structure of the Jacobian. To manipulate the eigenvalues to the necessary configuration requires the coordinated manipulation of at least two system parameters to a precise combination of values. Consequently, the chance of finding the right combination of parameters is much smaller for the more complex eigenvalue configurations corresponding to higher order bifurcations and more complicated nonlinear dynamics than it is for Hopf bifurcation which often results from manipulating only one parameter. Using the concepts presented above, one can generalize substantially the important contribution made by Scheintuch and Schmitz [1] some years ago. They pointed out that, in searching for models of catalytic reaction systems that exhibit oscillations, one should look for model structures and parameter values which admit Hopf bifurcation. Using the models outlined above, one can now look directly for model structures and corresponding parameter values which give the local structure corresponding to certain types of more complex dynamics.

Another difficulty awaits here which has also an analog in the simple Hopf case. In the case of subcritical Hopf bifurcation, as the steady state becomes unstable, the resulting limit cycle is unstable. Whether a Hopf bifurcation is supercritical or subcritical may be found using Floquet theory [19]. Similar difficulties arise for higher order bifurcations as for example G_1 bifurcation. Close to G_1 chaos is possible, but there is no guarantee that chaotic oscillations will occur. Unfortunately, unlike the Hopf case, the theory for G_1 bifurcation is not yet developed to the point where sufficient conditions are known for appearance of chaotic dynamics. Hopefully, the point is clear that the methods described here are intended as useful engineering guidelines and not as a rigid and strict mathematical structure.

Another point that was mentioned before in passing is also emphasized here. The discussion above is couched in terms of characteristic equation or Jordan block parameters, not system parameters. There is no guarantee in general that manipulation of a certain number of system parameters will influence a like number of Jordan block parameters in independent ways. Thus, for a given model, it may take manipulaton of three parameters to achieve an eigenvalue structure which can be obtained by manipulation of only two coefficients in the characteristic equation. In some systems which do not possess appropriate structure, it will not be possible to obtain certain eigenvalue configurations for any choice of any number of system parameters within the domains prescribed by physical limitations (e.g. non-negative rate constants). The question of the mapping from system parameters to coefficients of the characteristic equation is one that is amenable to direct and exact analysis for each particular model and which will not be addressed further here.

NOMENCLATURE

$\tilde{A},\tilde{B},\tilde{C},\tilde{D},\tilde{Z},\tilde{Z}'$: Chemical species in Ex. 1 (Eqn. 14).

$[\tilde{A}]^o,[\tilde{B}]^o$: Inlet concentration in Ex. 1.

$\hat{A},\hat{B},\hat{C}$: Species in Ex. 2.

A,A',C,B°,X°: Matrices in Appendix (Eqn. A.1).

B,C,D: Matrices defined in Eqn. (4).

b_1,b_2,b_3: Feedback parameters in Ex. 1, defined by Eqn. (20).

B_o°: Defined in Appendix.

ε_1: $\hat{k}_1'\cdot[\hat{B}]_M^{\hat{n}}\bar{t}_R$.

ε_2: $\hat{k}_2'\cdot[\hat{B}]_M^{\hat{n}}\cdot\bar{t}_R/[\hat{A}]_M^{\hat{m}}$.

C: Space of complex numbers.

d_1,d_2: Coupling constants in Ex. 2.

D_1,F_1,G_1: Types of bifurcation (Table I)

E^P: P-dimensional Euclidean space.

f: Function in Eqn. (1).

f_1: $d_1\bar{t}_R$.

f_2: $d_2\bar{t}_R$.

g: Function defined in Eqn. (2).

g°: $[A]^{\hat{m}}/[B]^{\hat{n}} = [A]_M^{\hat{m}}/[B]_M^{\hat{n}}$.

h',h'': Functions defined in Eqns. (6).

I: Identity matrix.

$\mathcal{J}$: Jacobian defined in Eqn. (4).

K', K'': Sets of eigenvalues defined in text.

$\tilde{k}_i$: Rate constants in Ex. 1.

k_i: Rate constants in Ex. 2, reactor I.

k_i': Rate constants in Ex. 2, reactor II.

l: Vector of integers.

l_k: Integers.

M: Parameter space in Appendix.

m^*: Dimension of space M.

m: Dimension of y.

n: Dimension of vector x.

n_e: Defined in Appendix.

n_i: Dimensionality of Jordan blocks in the Appendix.

P_o: Jordan upper triangular matrix in Appendix.

P_1, P_2: Parameters in discussion section.

R: Real numbers.

s: Defined in Eqn. (8).

t: Time.

$\tilde{t}_R$: Reactor residence time in Ex. 2.

u_A: 1.

u_B: $[\tilde{B}]^o/[\tilde{A}]^o$.

θ: $[\hat{B}]_{II}/[\hat{B}]_{I}$.

x: State variable vector in Eqn. (1).

x', x'': Variable vectors defined in Eqn. (5).

X, X': Functions defined in Eqns. (5).

χ: $[\tilde{A}]/[\tilde{A}]^{o}$.

x_s, y_s, z_s: Steady state values for Ex. (1).

x_s, y_s, z_s, θ_s: Steady state values in Ex. (2).

ζ: $[\hat{A}]_{II}/[\hat{A}]_{I}^{o}$.

x^{o}, y^{o}: Real and imaginary parts of eigenvalue in Appendix.

y: Transformed variables vector in Eqn. (2).

y', y'': Variables vector defined in Eqns (6).

Y: Function defined in Eqn. (7).

ψ: $[\tilde{B}]/[\tilde{A}]^{o}$.

ψ: $[\hat{B}]_{II}/[\hat{B}]_{I}^{o}$.

ζ: $[\tilde{C}]/[\tilde{A}]^{o}$.

ζ: $[\hat{A}]_{II}/[\hat{A}]_{I}$.

Subscripts I and II in Example 2 refer to reactors 1 and 2, respectively.

GREEK SYMBOLS

α_i: Coefficients of characteristic Eqn. (8).

α_1: $\tilde{k}_1\tau[\tilde{A}]^0$.

α_2: $\tilde{k}_2\tau[\tilde{A}]^0$.

β_1: $\tilde{k}_1[\tilde{B}]^p\tilde{\tau}_2$.

β_2: $\tilde{k}_2[\tilde{B}]^p\tilde{\tau}_2/[A]^p$.

α_i^0: Eigenvalues in Appendix.

β: Vector of parameters in Appendix.

β^0: Defined in Appendix.

ε_i: Eigenvalue.

ε_0: Eigenvalue at resonance.

λ_i: Eigenvalues.

λ_i^0: Complex parameters in Appendix.

Λ: Parameter space in Appendix.

μ: Parameter vector in Appendix.

ν: Parameter in Eqn. (1).

ρ_1, τ_1: Real and imaginary parts of complex parameters λ_i^0 in Appendix.

τ: Reactor residence time in Ex. 1.

φ: Transformation function defined in Eqn. (3).

φ^0: Mapping defined in Appendix.

ω: Imaginary part of eigenvalue [see Eqn. (10)].

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APPENDIX:

BIFURCATION JORDAN BLOCK STRUCTURE: ARNOLD'S VERSAL FAMILIES

The central concern in this section is the number of parameters that must be manipulated to achieve a particular Jordan block structure of the system Jacobian. Of course, the structures of interest are the somewhat atypical Jordan forms which correspond to the different bifurcation strata. Central to this discussion is a general parametric representation of matrices due to Arnold [26].

The analysis begins with the assumption that a particular system bifurcates in a particular stratum for some choice of system parameters and corresponding reference steady state. Specification of the presumed bifurcation stratum specifies simultaneously the Jordan form structure of the Jacobian at bifurcation. Arnold's theory is then applied to formulate a general representation of the Jordan matrix structure in the neighborhood (with respect to system parameter changes) of the Jordan matrix at bifurcation. Finally, assuming that system parameters are near the values which give bifurcation, the general parametric structure of the Jacobian Jordan form is examined to determine the number of parameters which must be adjusted to particular values or signs to obtain the Jordan matrix at bifurcation.

First the subject of miniversal deformation of matrices must be presented. Consider a family of matrices $A(\beta)$, complex in general, depending on a vector of complex parameters $\beta \in \Lambda \subset C^l$. For β close to β_o, the matrices $A(\beta)$ are called deformations of some particular matrix $A(\beta_o) \triangleq A_o$. A deformation $A'(\beta)$ of the matrix A_o is said to be equivalent to a deformation $A(\beta)$ if a nonsingular matrix $C(\beta)$ exists such that

$$A'(\beta) = C(\beta)A(\beta)[C(\beta)]^{-1} . \tag{A.1}$$

Let $\varphi^o: \Lambda \to M$ be a mapping ($M \subset C^m$ and $\Lambda \subset C^l$).

The family induced from $A(\beta)$ by the mapping φ° is the family $A(\varphi^\circ(\beta))$. A deformation $A(\beta)$ of a matrix $A_\circ$ is said to be *versal* if any deformation $A''(\mu)$ of the matrix $A_\circ$ is equivalent to a deformation induced from $A(\beta)$. A versal deformation is said to be *miniversal* if the dimension of the parameter space A (i.e. l) is the smallest possible for a versal deformation.

Denote by α_i° the eigenvalues of the matrix $A_\circ$ and let $n_1(\alpha_i^\circ) \geq n_2(\alpha_i^\circ) \geq \cdots$ be the dimensions, in decreasing order, of the Jordan blocks corresponding to α_i°. The smallest number of parameters for a miniversal deformation of the matrix $A_\circ$ is [26]

$$\sum_i [n_1(\alpha_i^\circ) + 3n_2(\alpha_i^\circ) + 5n_3(\alpha_i^\circ) + \cdots] . \tag{A.2}$$

A miniversal deformation of the matrix $P_\circ$, the Jordan upper triangular matrix of $A_\circ$, is

$$P_\circ + B^\circ(\beta) , \tag{A.3}$$

where $B^\circ(\beta)$ is a block-diagonal matrix whose blocks correspond to the eigenvalues of $A_\circ$. Each block B_i° corresponding to α_i° has all zero entries except in the positions indicated in Figure A1.

In chemical engineering one usually deals with real matrices. Versal deformations for real matrices have been constructed by Galin [30]. Assume that a real matrix has a complex conjugate pair of eigenvalues $x^\circ \pm iy^\circ$, with Jordan blocks of dimension $n_1 \geq n_2 > \cdots$ with $\sum n_i = n_\circ$. The part of the Jordan matrix that corresponds to the eigenvalues $x^\circ \pm iy^\circ$ may be writtten as:

$$B_\circ^\circ = \begin{bmatrix} X^\circ & -I \\ I & X^\circ \end{bmatrix} \tag{A.4}$$

where X° is the upper triangular real Jordan matrix with eigenvalue x° and blocks of dimensions $n_1 \geq n_2 > \cdots$ and I is the identity matrix of order $n_\circ$. It is true that the miniversal deformation of the decomplexified matrix is the same as the decomplexification of the miniversal deformation of the complex matrix [26]. This

allows determination of the miniversal deformation of the decomplexified (real) matrix using Arnold's theory for complex matrices. These facts are used next to determine the minimum number of parameters to realize different bifurcational Jordan matrix structures.

i. D_1 Bifurcation

Since a zero eigenvalue corresponds to a simple, one-dimensional Jordan block, it is clear that variation of one parameter is sufficient.

ii. D_2 Bifurcation (Hopf)

In complex form we seek to obtain the Jordan block for $i\omega$. It takes one complex parameter $\beta_1^c = \rho_1 + i\tau_1$ to do that. In real form one seeks to realize the structure [recall Eqn. (A.4)]

$$\begin{bmatrix} 0 & -\omega \\ \omega & 0 \end{bmatrix} \tag{A.5}$$

This has the following miniversal deformation:

$$\begin{bmatrix} \rho_1 & -\tau_1 \\ \tau_1 & \rho_1 \end{bmatrix}. \tag{A.6}$$

Thus one needs two real parameters. To ensure zero real part, ρ_1 is required. However, the other parameter τ_1 can be anything positive. Thus, variation of a single real parameter may produce Hopf bifurcation if it so happens that $\tau_1 > 0$. It might also take in other cases variation of two parameters, ρ_1 and τ_1, to assure Hopf bifurcation.

iii. F_1 Bifurcation

In this case, one seeks to obtain the structure:

$$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}. \tag{A.7}$$

As in the D_1 case, a miniversal deformation is the same for the complex and the real cases. It is here

$$\begin{bmatrix} 0 & 0 \\ \beta_1^* & \beta_2^* \end{bmatrix}. \tag{A.8}$$

where β_1^* and β_2^* are real parameters. Thus, manipulation of two real parameters is required to obtain this structure.

iv. F_2 Bifurcation

The structure to be achieved in this case is

$$\begin{bmatrix} 0 & -\omega & 0 \\ \omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{A.9}$$

which has miniversal deformation given by

$$\begin{bmatrix} \rho_1 & -\tau_1 & 0 \\ \tau_1 & \rho_1 & 0 \\ 0 & 0 & \rho_2 \end{bmatrix}. \tag{A.10}$$

Similarly to the D_2 case, it takes at least two real parameters (ρ_1 and ρ_2); a third parameter may be required to ensure $\omega > 0$.

v. F_3 Bifurcation

The structure to be obtained is

$$\begin{bmatrix} 0 & -\omega_1 & 0 & 0 \\ \omega_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\omega_2 \\ 0 & 0 & \omega_2 & 0 \end{bmatrix}. \tag{A.11}$$

with the miniversal deformation

$$\begin{bmatrix} \rho_1 & -\tau_1 & 0 & 0 \\ \tau_1 & \rho_1 & 0 & 0 \\ 0 & 0 & \rho_2 & -\tau_2 \\ 0 & 0 & \tau_2 & \rho_2 \end{bmatrix}. \tag{A.12}$$

Thus at least two real parameters ρ_1 and ρ_2 are required. In some cases up to four

(ρ_1, ρ_2, τ_1 and τ_2) may be needed to ensure $\omega_1 > 0$, $\omega_2 > 0$.

vi. G_1 Bifurcation

One seeks to realize the structure

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} . \tag{A.13}$$

As in the D_1 and F_1 cases, the complex and real miniversal deformations coincide. The miniversal deformation is

$$\left\{ \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \beta_1^* & \beta_2^* & \beta_3^* \end{bmatrix} : \beta_1^*, \beta_2^*, \beta_3^* \text{ real} \right\} . \tag{A.14}$$

Thus, it takes three real parameters, at least, to obtain the G_1 bifurcation structure.

It is clear that the results obtained via the method of characteristic equations is totally consistent with the theory of versal families of matrices. The latter approach is more complete in that it considers Jordan block structures characteristic of different bifurcation strata. Obtaining corresponding eigenvalue configurations via analysis of the characteristic equation is a necessary but not sufficient condition for achieving particular Jordan matrix structure. Degenerate cases in which the desired eigenvalue structure does not yield the desired Jordan block structure are sufficiently unusual, however, so that the simpler approach based on the characteristic equation is usually adequate for locating various bifurcation strata.

TABLE CAPTIONS

Table I: Summary of the properties of the system Jacobian at the reference steady-state for different bifurcation types (strata). Eigenvalues in left-hand plane and corresponding Jordan blocks are not shown. For Jordan block structure for the cases $G_2 - G_5$ see *Ref.* [7,26]. Right column indicates when steady-state bifurcation is possible.

Table II: Steady-state and eigenvalue structure as a function of coupling parameters for Example II.

Table I

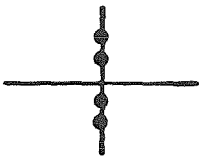
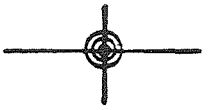
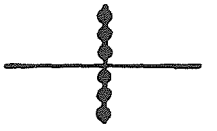
BIFURCATION TYPE	JACOBIAN JORDAN BLOCK STRUCTURE	JACOBIAN EIGENVALUE STRUCTURE	POSSIBLE STEADY STATE BIFURCATION
D_1	$\begin{bmatrix} 0 \end{bmatrix}$		YES
D_2	$\begin{bmatrix} 0 & -\omega \\ \omega & 0 \end{bmatrix}$		NO
F_1	$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$		YES
F_2	$\begin{bmatrix} 0 & \omega & 0 \\ \omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$		YES
F_3	$\begin{bmatrix} 0 & -\omega_1 & 0 & 0 \\ \omega_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\omega_2 \\ 0 & 0 & \omega_2 & 0 \end{bmatrix}$		NO
G_1	$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}$		YES
G_2	–		NO
G_3	–		YES
G_4	–		YES
G_5	–		NO

Table II

Steady-state and eigenvalue structure as a function of coupling parameters for Example II

ℓ_1	ℓ_2	Steady State	Eigenvalues
0.01	0.01	x = 0.250168 y = 1.580007 z = 0.210119 w = 1.939946	1.232053 ± 3.898084i 0.407089 ± 4377235i
0.01	0.1	x = 0.248421 y = 1.587432 z = 0.211338 w = 1.932228	1.159853 ± 3.992019i 0.387768 ± 4.407187i
0.1	0.01	x = 0.251668 y = 1.569634 z = 0.208914 w = 1.951186	1.198648 ± 3.797853i 0.346962 ± 4.351923i
0.1	1.0	x = 0.237587 y = 1.633455 z = 0.270524 w = 1.882123	0.841447 ± 4.190754i -0.289672 ± 5.074837i

FIGURE CAPTIONS

Figure 1: Venn diagram showing relationships between bifurcation strata and local system dynamic features near bifurcation. The indicated strata correspond to Jacobian matrices at the reference steady state with up to three eigenvalues on the imaginary axis.

Figure 2: Decrement diagram for Example I.

Figure 3: Regions of the coupling parameter space corresponding to different classes of system behavior (Example II).

Figure 4: Dimensionless concentration trajectories for coupled CSTRs with autocatalytic reactions (Example II; coupling parameters: $f_1 = 0.01$, $f_2 = 0.01$).

Figure 5: System dynamics for autocatalytic reactions in coupled CSTRs (Example II; coupling parameters: $f_1 = 0.01$, $f_2 = 0.1$).

Figure 6: Dynamic behavior of coupled CSTRs with isothermal autocatalytic reactions (Example II; coupling parameters: $f_1 = 0.1$, $f_2 = 0.01$).

Figure A1: Form of the matrix B in the miniversal deformation of Eqn. (A.3). Different parameters appear at the positions indicated in each block B_i corresponding to the eigenvalue α_i°. Alternative forms for the B matrix are presented by Arnold [28].

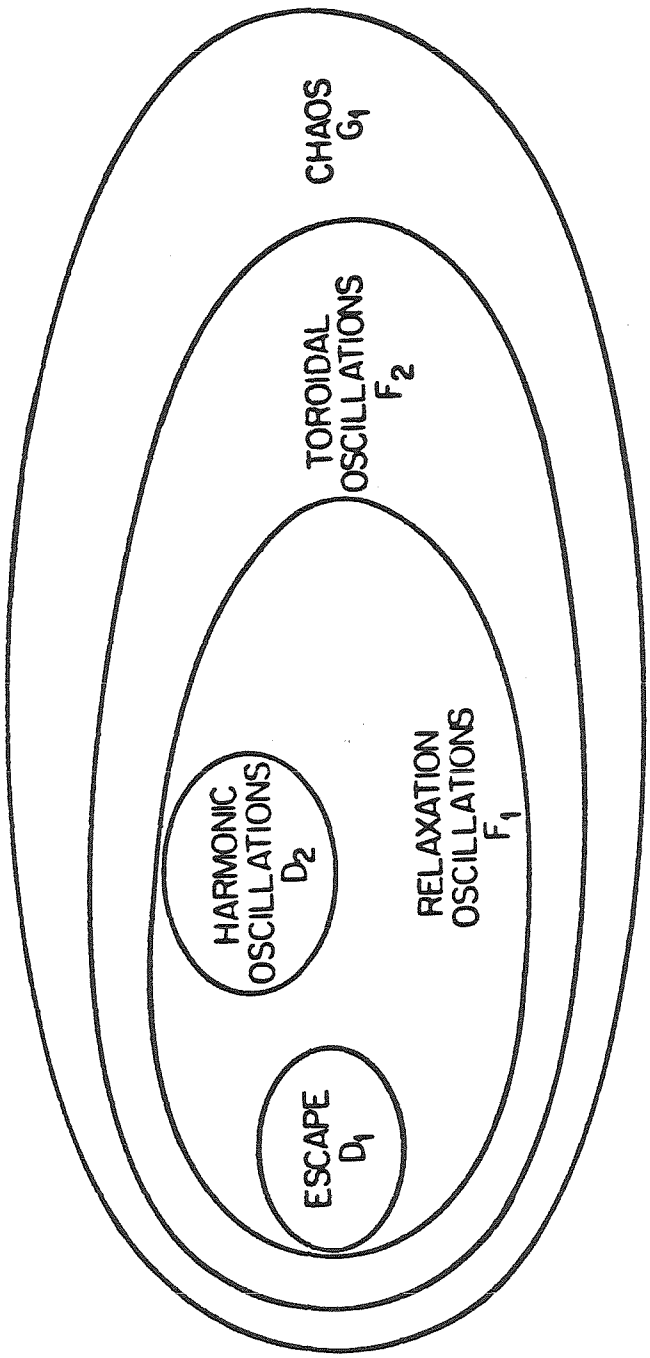

CHAOS
G_1
TOROIDAL
OSCILLATIONS
F_2
RELAXATION
OSCILLATIONS
F_1
HARMONIC
OSCILLATIONS
D_2
ESCAPE
D_1

FIGURE 1

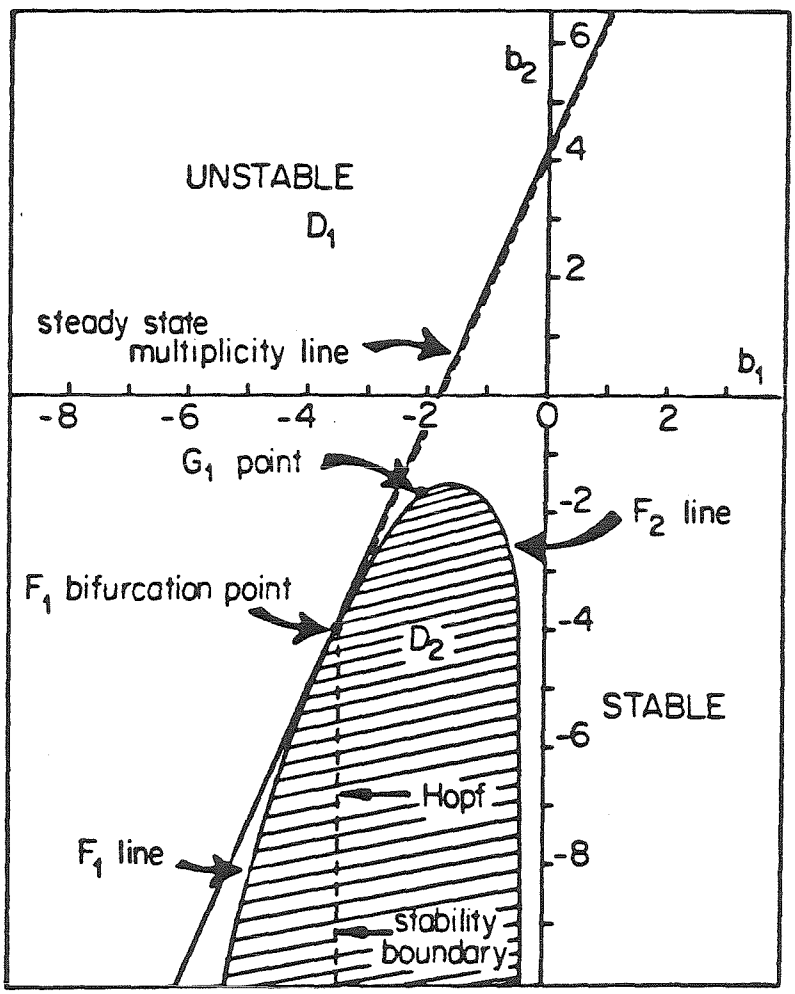

b_2
6
4
2
UNSTABLE
D_1
steady state
multiplicity line
b_1
-8
-6
-4
-2
0
2
G_1 point
-2
F_2 line
F_1 bifurcation point
D_2
-4
STABLE
-6
Hopf
F_1 line
-8
stability
boundary

FIGURE 2

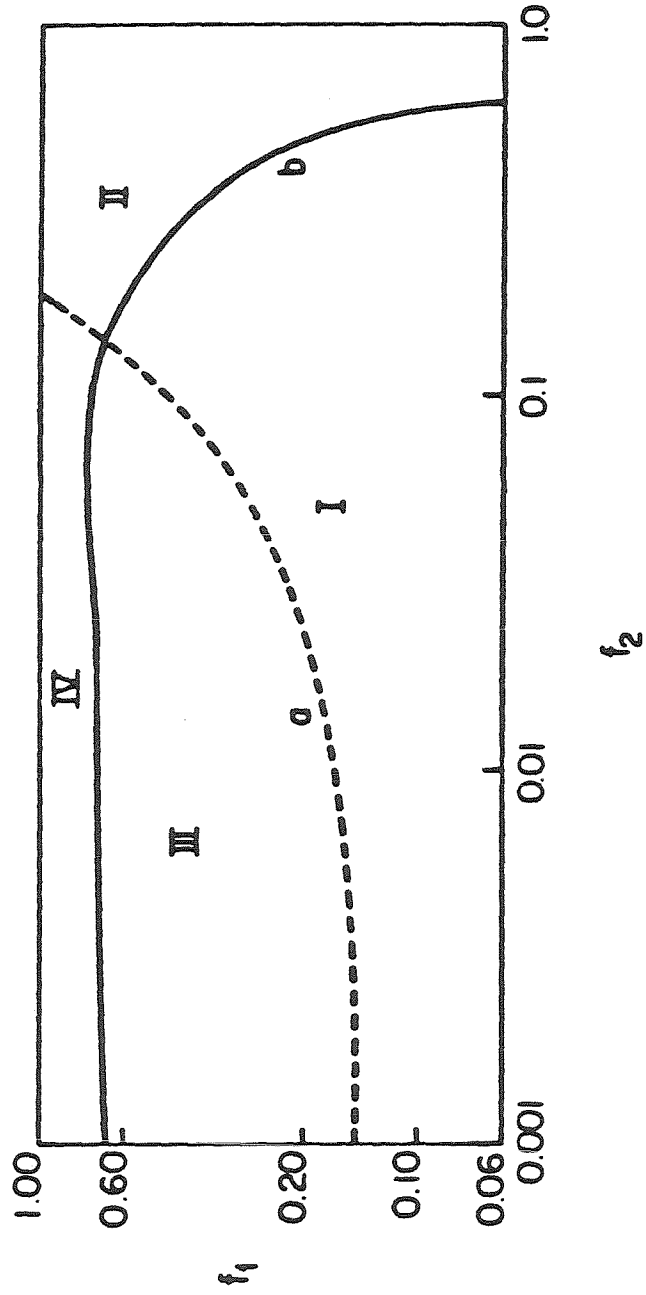


FIGURE 3

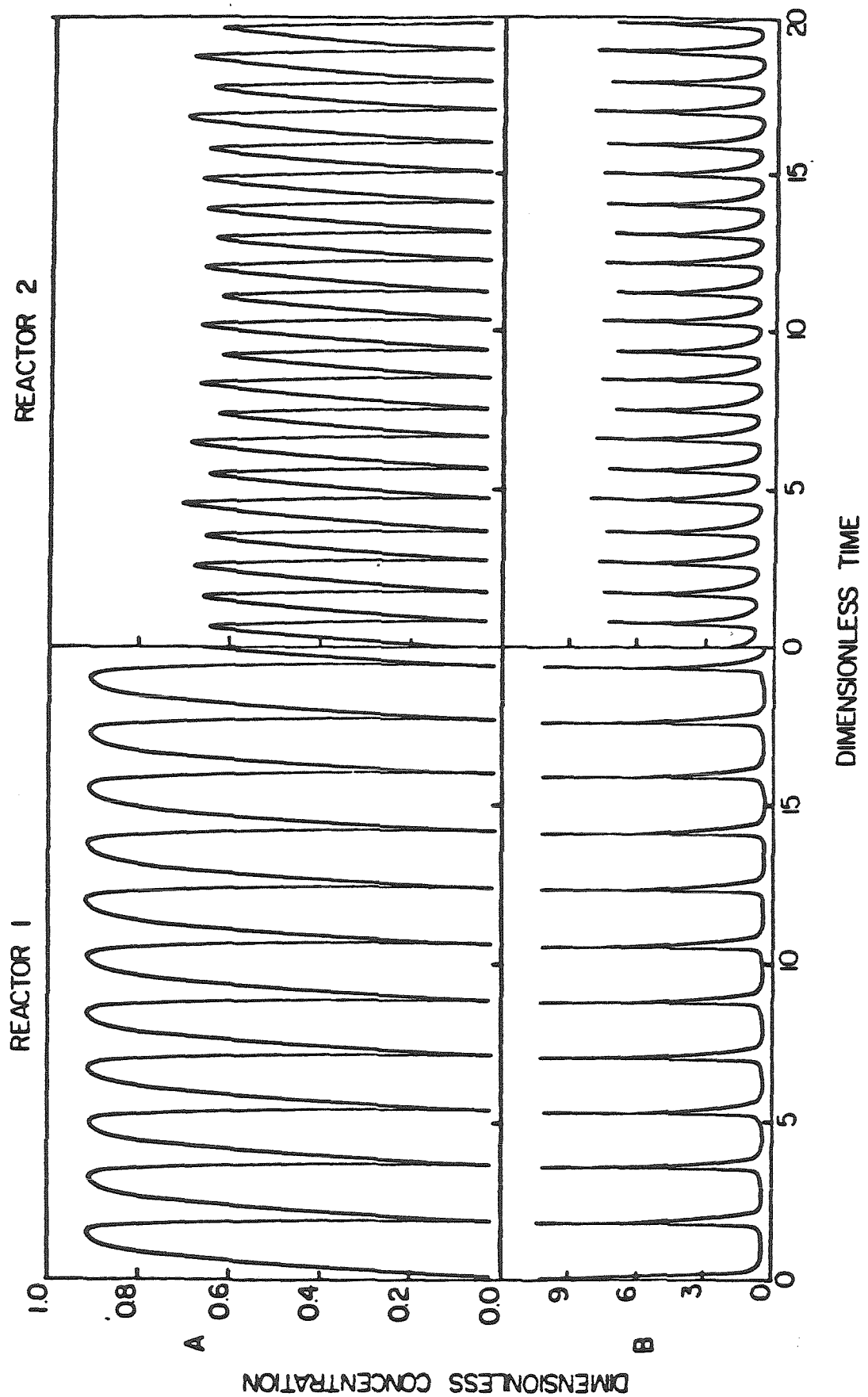

REACTOR 1
REACTOR 2
A
B
DIMENSIONLESS CONCENTRATION
DIMENSIONLESS TIME
1.0
.8
0.6
0.4
0.2
0.0
9
6
3
0
0
5
10
15
20

FIGURE 4

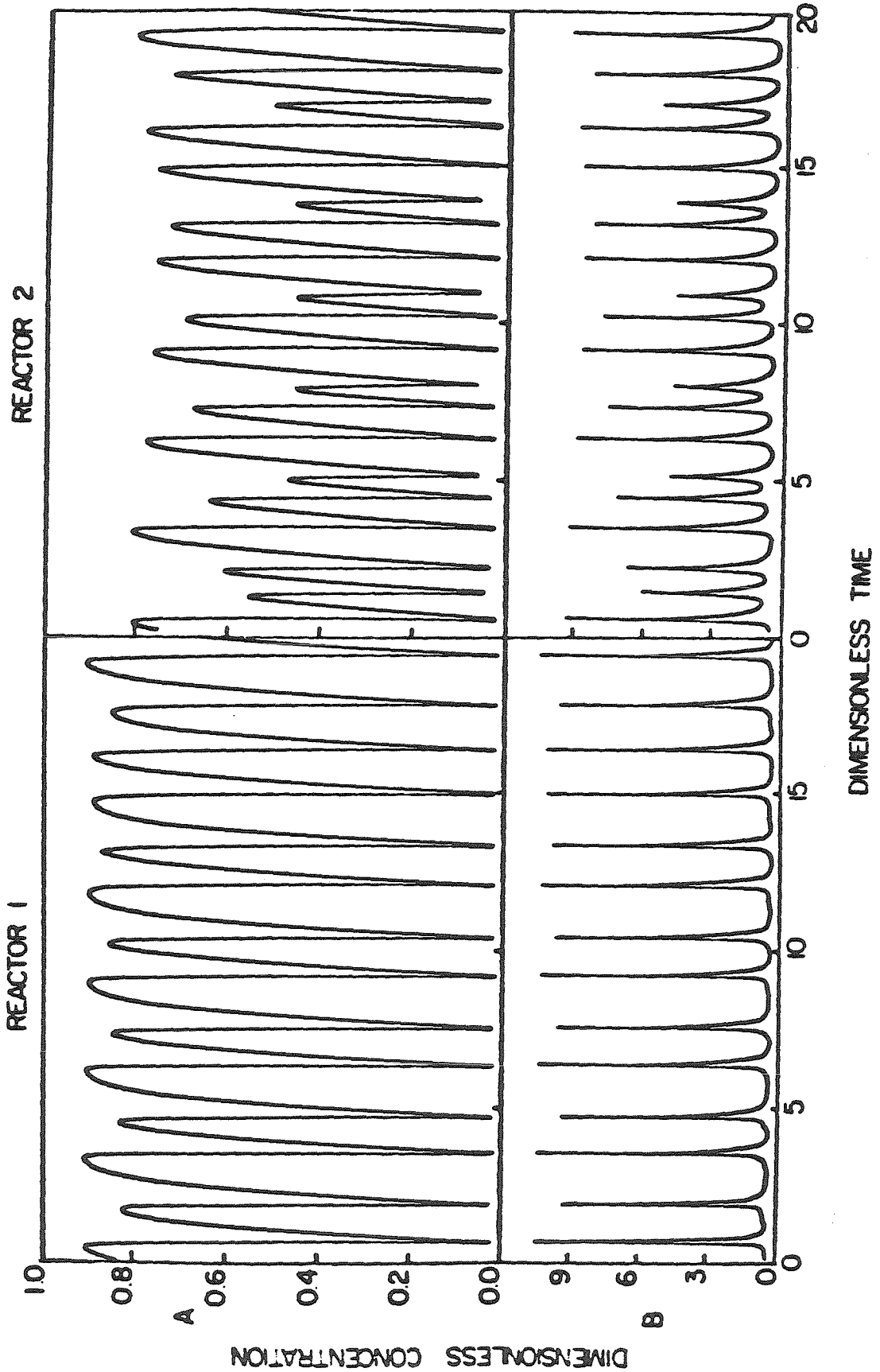

REACTOR 1
REACTOR 2
A
B
DIMENSIONLESS CONCENTRATION
DIMENSIONLESS TIME
1.0
0.8
0.6
0.4
0.2
0.0
9
6
3
0
0
5
10
15
0
5
10
15
20

FIGURE 5

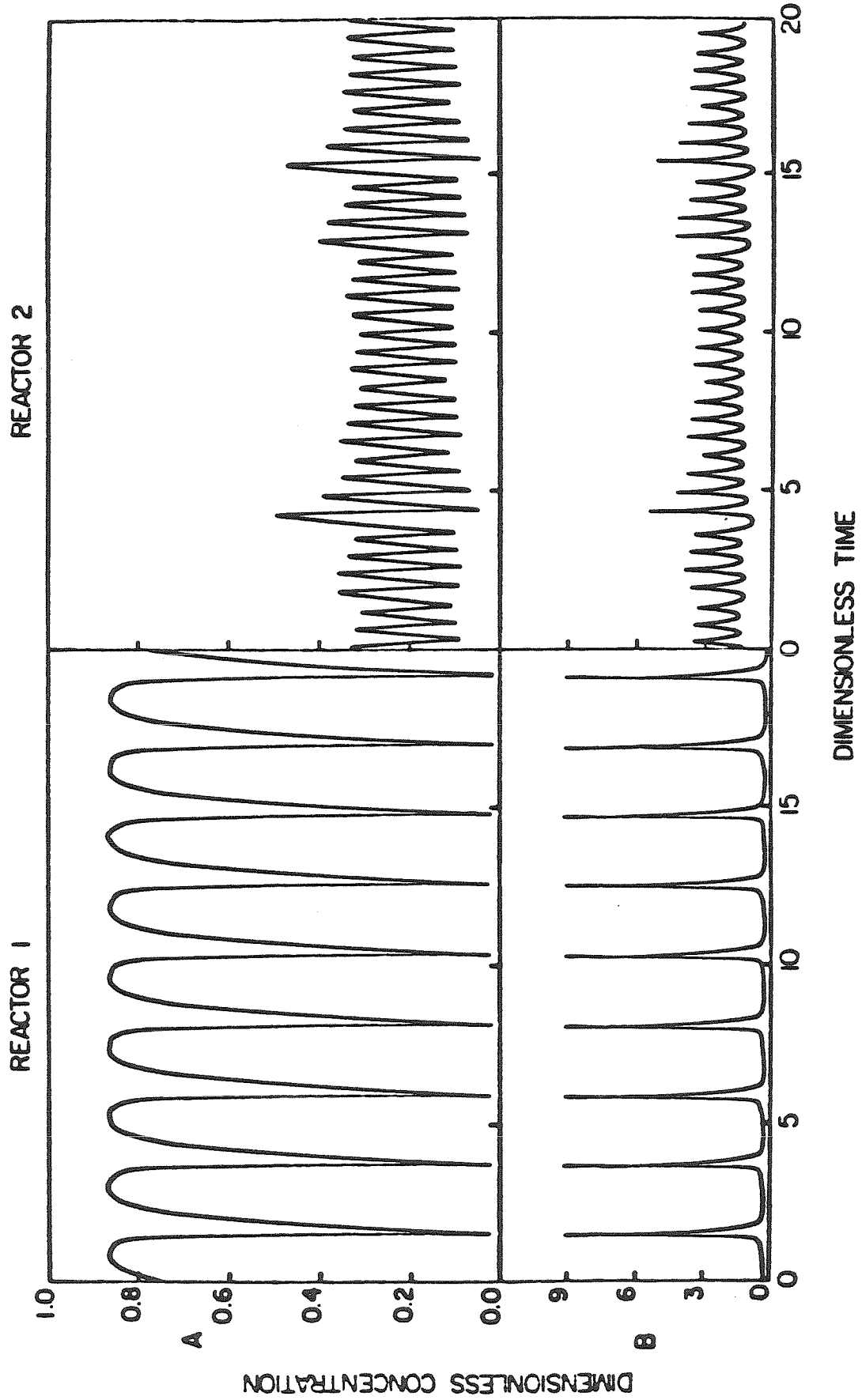

REACTOR 1
REACTOR 2
A
B
DIMENSIONLESS CONCENTRATION
DIMENSIONLESS TIME
1.0
0.8
0.6
0.4
0.2
0.0
9
6
3
0
0
5
10
15
20

FIGURE 6

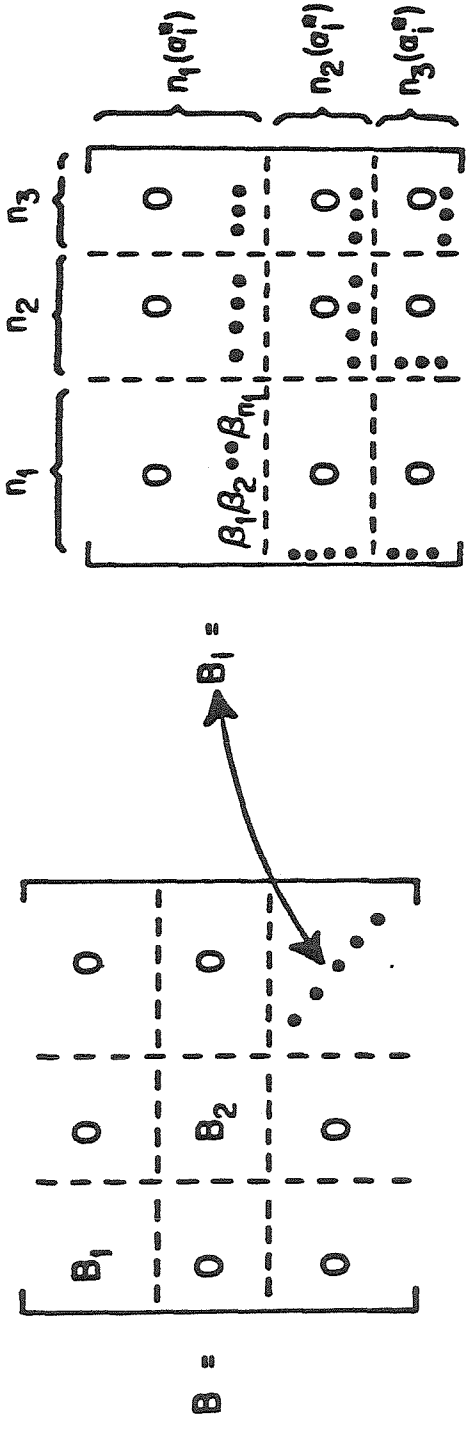


FIGURE A1

CHAPTER 5 : NORMAL FORMS FOR CHEMICAL REACTION SYSTEMS VIA THE AFFINE TRANSFORMATION

INTRODUCTION

In a previous publication [1], the notion of normal forms of dynamic systems was reviewed. The *normal form* is a simpler form of the system model equations that retains all relevant information regarding dynamic behavior in the neighborhood of a system steady state. Substantial effort has been invested by mathematicians to find the normal form of dynamic systems after perturbation from a point of bifurcation [e.g. 2,3]. When at bifurcation, a system's dynamic behavior is absolutely nonlinear even locally. The advantage of studying a system close to bifurcation is the opportunity to identify the qualitative nature of its nonlinear dynamic characteristics by local analysis.

In general, converting a dynamic system to its normal form is a very complicated and practically untenable procedure, at least until a general computer code is developed for this purpose. In this work a different type of normal form is introduced, and the class of problems that are reducible to this normal form via a simple transformation is identified. A specific algorithm for converting such systems to this normal form is given. After transformation to the normal form following the given algorithm, one can identify which parameters can be varied independently to affect the system's dynamic behavior and which groupings of parameters appear in the normal form.

Next, it is observed that this normal form coincides in the cases of F_1 and G_1 bifurcation [1] with the classical normal form. A certain notion of codimension is defined and the effect of perturbing a system from the F_1 bifurcational structure is studied. A chemical example due to Eigenberger [4] is treated as a perturbed F_1 system. An enzyme-catalyzed reaction sequence with feedback regulation of the initial reaction, first considered by Walter [5], is also investigated using the methods developed herein.

THE AFFINE TRANSFORMATION: REDUCTION TO THE COMPANION NORMAL FORM

Consider a dynamic system of the form:

$$\frac{d\mathbf{x}}{dt} = A\mathbf{x} + \hat{b}f(\mathbf{x}) + \hat{c} \tag{1}$$

where

$$A = \begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \hat{c}_1 & \hat{c}_2 & \cdot & \cdot & \cdot & \hat{c}_n \end{bmatrix} \tag{2}$$

$$\hat{b} = [0 \ \cdots \ 0 \ 1]^T \tag{3}$$

$$\hat{c} = [0 \ \cdots \ 0 \ \hat{d}]^T \tag{4}$$

The Jacobian for this system has the following form:

$$J = \begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \left[\hat{c}_1 + \frac{\partial f}{\partial x_1}\right] & \cdot & \cdot & \cdot & \cdot & \left[\hat{c}_n + \frac{\partial f}{\partial x_n}\right] \end{bmatrix} \tag{5}$$

and the steady states are

$$x_{2s} = x_{3s} = \cdots = x_{ns} = 0 \tag{6}$$

with x_{1s} given by

$$f(x_{1s},0,0, \ \cdots \ ,0) + \hat{c}_1 x_{1s} + \hat{d} = 0 \ . \tag{7}$$

The characteristic equation of the Jacobian then is [6]

$$s^n - \left[\hat{c}_n + \frac{\partial f}{\partial x_n}(x_{1s},0, \ \cdots \ ,0)\right]s^{n-1} - \cdots - \left[\hat{c}_1 + \frac{\partial f}{\partial x_1}(x_{1s},0, \ \cdots \ ,0)\right] = 0 \ . \tag{8}$$

Balakotaiah and Luss [7] have used Golubitsky's theory [8] to study bifurcations of steady states when reduction to a single algbraic equation is possible. Different bifurcation diagrams are obtainable depending on the "order of contact" of the one-

dimensional function at the bifurcation point. In this procedure of reducing the dimensionality, care must be taken that no new steady states which are not steady states of the original system are introduced. For systems that can be reduced to the form of Eqn. (1), this possible pitfall is definitely avoided. Another convenient property of systems of the form (1) is that the characteristic equation is trivially obtained in the form of Eqn (8). In general, finding the characteristic equation of a large dimensional system involves considerable algebraic effort.

In addition to obtaining a single equation for studying the steady states of the system, one can identify easily conditions for different bifurcation phenomena [3]. Which system parameters can be varied independently to produce certain steady-state multiplicity and eigenvalue structure are revealed explicitly. For low-dimensional systems it is easy to reach conclusions about the effect of system parameters in realizing certain bifurcations. In addition, analysis of Eqn. (1) shows directly how changing a parameter perturbs the system to a certain "structurally stable" Jacobian eigenvalue configuration. These attributes of models of form (1) will be illustrated in the examples which follow.

The opportunities for analysis of system models of form (1), which is called the *companion normal form*, motivate a search for the class of systems that are reducible to this form. The transformation should not introduce additional steady states and should retain the system's eigenvalue configuration. One such transformation is

$$\mathbf{y} = \mathbf{S}\mathbf{x} + \mathbf{g} \ . \tag{9}$$

Such a change of variables, an *affine transformation*, transfers the origin and rotates and expands (contracts) the system coordinates, but it does not affect the steady-state multiplicity and the eigenvalue structure.

Solving for $\mathbf{x}$ in Eqn. (9) and substituting into Eqn. (1),

$$\frac{dy}{dt} = SAS^{-1}y + S\hat{b}f\left[S^{-1}(y-g)\right] + S\hat{c} - SAS^{-1}g\,. \tag{10}$$

Thus a system reducible to the form of Eqn. (1) by the affine transformation Eqn. (9) must have the form:

$$\frac{dy}{dt} = Ky + Ah(y) + m \tag{11}$$

where $h(y)$ is a function from R^n to R. Accordingly, the system must have a single nonlinearity, possibly appearing in more than one of the state equations. One then identifies similar coefficients in Eqns. (10) and (11), which gives the following relationships:

$$K = SAS^{-1} \Leftrightarrow A = S^{-1}KS \tag{12.1}$$

$$A = S\hat{b} \Leftrightarrow S^{-1}A = \hat{b} \tag{12.2}$$

$$m = Sc - Kg\,. \tag{12.3}$$

An algorithm for transforming system (11) to the companion normal form (1) is given next: form the matrix S^{-1} as follows,

$$S^{-1} = \begin{bmatrix} \tilde{f} \\ \tilde{f}K \\ \vdots \\ \tilde{f}K^{n-1} \end{bmatrix} \tag{13}$$

where $\tilde{f}$ is any row vector that makes S^{-1} nonsingular. Then

$$S^{-1}A = \hat{b} \tag{14}$$

is a linear equation in $\tilde{f}_1, \cdots, \tilde{f}_n$ that must be satisfied. This uniquely determines the vector $\tilde{f} = (\tilde{f}_1, \cdots, \tilde{f}_n)$ and hence the matrix S^{-1}. Then, from Eqn. (12.3)

$$g = K^{-1}[S\hat{c} - m]\,. \tag{15}$$

Since

$$\mathbf{Sc} = \hat{\mathbf{d}} \begin{bmatrix} S_{1n} \\ \cdot \\ \cdot \\ S_{nn} \end{bmatrix} = \hat{\mathbf{d}}\mathbf{\Lambda} \tag{16}$$

one can choose:

$$\mathbf{g} = \mathbf{K}^{-1}[\hat{\mathbf{d}}\mathbf{\Lambda} - \mathbf{m}] \tag{17}$$

for any $\hat{\mathbf{d}}$ and hence for $\hat{\mathbf{d}}$=0 in particular. Thus it is sufficient to set:

$$\mathbf{g} = -\mathbf{K}^{-1}\mathbf{m}\,. \tag{18}$$

Then the transformation:

$$\mathbf{x} = \mathbf{S}^{-1}\mathbf{y} + \mathbf{S}^{-1}\mathbf{K}^{-1}\mathbf{m} \tag{19}$$

will transform system (11) to the form of Eqn. (1) with $\hat{\mathbf{d}}$=0.

EXAMPLE: ENZYMATIC REACTION SEQUENCE WITH FEEDBACK ALLOSTERIC REGULATION

Walter used Liapounov's direct method to obtain stability criteria for a generalized negative-feedback enzyme-catalyzed reaction sequence of the Yates-Pardee type [5]. The dynamic equations for this system are:

$$\dot{X}_o = \kappa E_o - (h_o + \kappa_o)X_o$$

.....

$$\dot{S}_i = \kappa_{i-1}X_{i-1} - H_iE_iS_i + h_iX_i - j_iS_i + j_{-i}$$

$$\dot{X}_i = H_iE_iS_i - (h_i + \kappa_i)X_i \quad i = 1,2,\cdots,n$$

.....

$$\dot{S}_{n+1} = \kappa_nX_n - \rho H_{n+1}E_oS_{n+1}^{\rho} + \rho h_{n+1}X_{n+1} - j_{n+1}S_{n+1} + j_{-(n+1)} \tag{20}$$

$$\dot{X}_{n+1} = H_{n+1}E_oS_{n+1}^{\rho} - h_{n+1}X_{n+1}$$

$$0 = \dot{E}_o + \dot{X}_o + \dot{X}_{n+1}$$

.....

$$0 = \dot{E}_i + \dot{X}_i \quad i = 1,2,\cdots,n$$

where S_i are substrates. S_{i+1} is produced from S_i under the catalysis of enzyme E_i via the enzyme-substrate complex X_i for i = 0,1,...,n.

The S_i (i = 0,1,...,n + 1) may exchange with the "exterior", but E_i and X_i (i = 0,1,...,n) are confined to the "interior" system. The parameters j_{-i} and j_i are the rate constants for the exchange of S_i to and from the "exterior", respectively. H_i (i = 0,1,...,n) is the bimolecular rate constant for combination of S_i and E_i; h_i and κ_i are the unimolecular rate constants for dissociation of X_i to S_i and E_i, and to S_{i+1} and E_i, respectively. It is assumed that E_o is inhibited cooperatively by ρ molecules of S_{n+1}; the "rate constant" for formation of the inhibited form of the enzyme X_{n+1} is S_{n+1} and the "rate constant" for dissociation of X_{n+1} to S_{n+1} and E_o is h_{n+1}. S_o is maintained constant by a large external reservoir and $\kappa = H_oS_o$.

Making the following set of assumptions:

i. $\dot{X}_i = 0$, (i = 0,1,...,n + 1)

ii. $S_i << {}^iK_m$, (i = 0,1,...,n)

iii. Terms beyond $(S_{n+1})^{\rho}$ in the expansion of $\tilde{b}_o/(1 + \alpha S_{n+1}^{\rho})$, where $\alpha = H_{n+1}/h_{n+1}$, can be neglected,

the model described above can be simplified to the following form:

$$\begin{aligned} \dot{S}_1 &= -\alpha\tilde{b}_o(S_{n+1})^{\rho} - (j_1 + \tilde{b}_1)S_1 + j_{-1} + \tilde{b}_o \\ \dot{S}_i &= \tilde{b}_{i-1}S_{i-1} - (j_i + \tilde{b}_i)S_i + j_{-i} \quad (i = 2,...,n+1) \end{aligned} \tag{21}$$

where

$$\tilde{b}_o = \frac{{}^oV_m S_o}{{}^oK_m + S_o}, \tilde{b}_i = \frac{{}^iV_m}{{}^iK_m}; (i = 1,2,....,n)$$

$$\tilde{b}_{n+1} = 0 \tag{22}$$

and where

$${}^iV_m = \kappa_i E_i(0) \; ; \; {}^iK_m = \frac{h_i + \kappa_i}{H_i};$$

$$E_i(0) = X_i + E_i \quad (i = 1,2,....,n) \; .$$

$$E_o(0) = X_o + E_o + X_{n+1} \; . \tag{23}$$

Setting

$$y_1 = S_{n+1} \; . \; y_2 = S_n \; . \; \cdots \; . \; y_{n+1} = S_1$$

$$b_i = \tilde{b}_{[(n+2)-i]}, \; a_i = -j_{[(n+2)-i]}; \quad i = 1,....,n+1$$

$$c_i = j_{-[(n+2)-i]}, \; i = 1,....,n \; ; \; c_{n+1} = j_{-1} + \tilde{b}_o \; , \; d = \alpha \tilde{b}_o \tag{24}$$

$$d_i = a_i - b_i \; ; \; i = 1,....,n+1 \; ,$$

the system may be written in the form of system (11) with

$$K = \begin{bmatrix} d_1 & b_2 & & \\ & d_2 & b_3 & 0 \\ & & & \\ & 0 & & b_{n+1} \\ & & & d_{n+1} \end{bmatrix} \tag{25}$$

$$\Lambda = [0 \; ..... \; 0 \; -d]^T \tag{26.1}$$

$$h(y) = y_1^{\alpha} \tag{26.2}$$

$$m = [c_1 c_2 \; \cdots \; c_{n+1}]^T \; . \tag{26.3}$$

Forming S^{-1} according to Eqn. (13) begins with calculation of

$$\underline{K}^i =$$

$$\begin{bmatrix}
d_1^i & b_2(d_1+d_2)^{i-1} & b_2b_3(d_1+d_2+d_3)^{i-2} & \cdots & (b_2b_3\cdots b_{i+1}) & 0 & 0 \cdots 0 \\
0 & d_2^i & b_3(d_2+d_3)^{i-1} & \cdots & \cdot & (b_3b_4\cdots b_{i+2}) & 0 \cdots 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & (b_{n+2-i}\cdots b_nb_{n+1}) \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\underline{0} & 0 & d_{n-1}^i & b_n(d_n+d_{n+1})^{i-1} & b_nb_{n+1}(d_{n-1}+d_n+d_{n+1})^{i-2} & & \\
\underline{0} & 0 & 0 & d_n^i & b_{n+1}(d_n+d_{n+1})^{i-1} & & \\
\underline{0} & 0 & 0 & 0 & d_{n+1}^i & &
\end{bmatrix}$$

(27)

Then

$$\tilde{f}K^i = \begin{bmatrix} \tilde{f}_1 d_1^i \\ \tilde{f}_1 b_2 (d_1 + d_2)^{i-1} + \tilde{f}_2 d_2^i \\ \tilde{f}_1 b_2 b_3 (d_1 + d_2 + d_3)^{i-2} + \tilde{f}_2 b_3 (d_2 + d_3)^{i-1} + \tilde{f}_3 d_3^i \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \tilde{f}_{n+1-i} b_{n+2-i} \cdots b_{n+1} + \cdots + \tilde{f}_n b_{n+1} (d_n + d_{n+1})^{i-1} + \tilde{f}_{n+1} d_{n+1}^i \end{bmatrix} \tag{28}$$

Substitution of Eqns. (3), (26.1) and (28) into Eqn. (14) and solving for the unknowns $\tilde{f}_i$ gives

$$\begin{aligned} \tilde{f}_{n+1} = \tilde{f}_n = \cdots = \tilde{f}_2 = 0 \,, \\ \tilde{f}_1 = - \frac{1}{d b_2 b_3 \cdots b_{n+1}} \,. \end{aligned} \tag{29}$$

The matrix S^{-1} can be written explicitly using (13),

$$S^{-1} = - \frac{1}{d b_2 \cdots b_{n+1}} \cdot$$

$$\cdot \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 & \cdots & 0 \\ d_1 & b_2 & 0 & \cdots & 0 & \cdots & 0 \\ d_1^2 & b_2(d_1 + d_2) & b_2 b_3 & & 0 & \cdots & 0 \\ d_1^3 & b_2(d_1 + d_2)^2 & b_2 b_3 (d_1 + d_2 + d_3) & b_2 b_3 b_4 & \cdots & & 0 \\ \cdot & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & & 0 \\ \cdot & \cdot & \cdot & \cdot & & & \\ d_1^n & b_2(d_1 + d_2)^{n-1} & b_2 b_3 (d_1 + d_2 + d_3)^{n-2} & \cdot & & & b_2 b_3 \cdots b_{n+1} \end{bmatrix} \tag{30}$$

The inverse of K may be evaluated analytically. Multiplying the result by m from Eqn. (26.3) gives

$$\mathbf{K}^{-1}\mathbf{m} = \begin{bmatrix} \dfrac{c_1}{d_1} - \dfrac{b_2c_2}{d_1d_2} + \dfrac{b_2b_3c_3}{d_1d_2d_3} + \cdots + (-1)^n \dfrac{b_2b_3 \cdots b_{n+1}c_{n+1}}{d_1d_2 \cdots d_{n+1}} \\ \dfrac{c_2}{d_2} - \dfrac{b_3c_3}{d_2d_3} + \cdots + \dfrac{(-1)^{n-1}\, b_3 \cdots b_{n+1}c_{n+1}}{d_2d_3 \cdots d_{n+1}} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \dfrac{c_n}{d_n} - \dfrac{b_{n+1}c_{n+1}}{d_nd_{n+1}} \\ \dfrac{c_{n+1}}{d_{n+1}} \end{bmatrix} \tag{31}$$

It will be convenient later to denote the first element of this vector by the (scalar) θ.

The required transformation to the companion normal form is now given by Eqn. (18) where $\mathbf{S}^{-1}$ is given by Eqn. (30) and $\mathbf{K}^{-1}\mathbf{m}$ by Eqn. (31). The matrix $\mathbf{A}$ may be evaluated by Eqn. (12.1). However, the complicated algebra implied there can be avoided. The first n rows of the $(n+1)\times(n+1)$ matrix $\mathbf{A}$ are known by the definition of the companion normal form, see Eqn. (2); only the last row need be evaluated. Equation (8) indicates that the entries of the last row of $\mathbf{A}$ are combinations of its eigenvalues. Since $\mathbf{A}$ and $\mathbf{K}$ are similar matrices [see Eqn. (12.1)], they have the same eigenvalues. By inspection of Eqn. (25), the eigenvalues of $\mathbf{K}$, an upper triangular matrix, are simply its diagonal elements $d_1, d_2, \cdots, d_{n+1}$. Combining these facts, the coefficient matrix of the companion normal form is given by Eqn. (2) with

$$\hat{c}_1 = (-1)^{n+1} \prod_{i=1}^{n+1} d_i$$

$$\cdots\cdots\cdots\cdots$$

$$\hat{c}_n = -\frac{1}{2} \sum_{\substack{[i,j = 1, \cdots, n+1 \\ i \neq j}} d_i d_j \tag{32}$$

$$\hat{c}_{n+1} = \sum_{i=1}^{n+1} d_i$$

Writing out the companion normal form in detail gives

$$\dot{x}_1 = x_2$$

$$\dot{x}_2 = x_3$$

.....

$$\dot{x}_{n+1} = (-db_2b_3 \cdots b_{n+1}x_1 - \theta)^\rho + (-1)^n \prod_{i=1}^{n+1} d_i x_1 + \cdots + \sum_{i=1}^{n+1} d_i x_{n+1} \tag{33}$$

The steady states are determined by:

$$g(x_1) = (-db_2b_3 \cdots b_{n+1}x_1 - \theta)^\rho + (-1)^n \prod_{i=1}^{n+1} d_i x_1 \tag{34}$$

and the corresponding Jacobian is:

$$J = \begin{bmatrix} 0 & 1 & 0 & \cdots & \cdots & \cdots & \cdots & & \\ 0 & 0 & 1 & \cdots & \cdots & \cdots & \cdots & & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & & \cdot \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & 0 & \cdot \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & & 1 \\ (-1)^{n+1} \prod_{i=1}^{n+1} d_i - (db_2 \cdots b_{n+1}\rho)(-db_2 \cdots b_{n+1}x_1 - \theta)^{\rho-1} & \cdots & & & & & & & \sum_{i=1}^{n+1} d_i \end{bmatrix} \tag{35}$$

One can see that the steady-state solutions and their eigenvalue configurations do not depend on all model parameters α_i, b_i and c_i (3n + 6 variables) independently. The whole system dynamics depend on (n + 4) combinations of the system parameters which have been explicitly identified; i.e. on ρ, θ, $d_1, \cdots, d_{n+1}$ and $db_2 \cdots b_{n+1}$. The transformation method described here has enabled reformulation of the original complicated system to the much simpler form of system (33), and it has been shown which combinations of the original system parameters independently influence its dynamics. Next are summarized analyses of the properties of the steady-state solution set and the dynamics of the regulated enzyme-catalyzed reaction sequence.

Consider first the steady-state problem. Letting

$$\mathcal{Z} \triangleq -db_2b_3 \cdots b_{n+1}x_1 - \theta \tag{36}$$

and

$$\alpha_o = \frac{(-1)^{n+1} \prod_{i=1}^{n+1} d_i}{db_2b_3 \cdots b_{n+1}}. \tag{37}$$

the steady-state Eqn. (34) may be rewritten

$$\tilde{z}^\rho + \alpha_o \tilde{z} + \alpha_o \theta = 0 \ . \tag{38}$$

From this equation is is clear that the number of steady-states depends only on the parameter ρ and on two combinations of the original system parameters, α_o and θ. It is very easy to see that for ρ even, the system can have zero, one or a maximum of two steady-states, whereas for odd ρ, one, two or a maximum of three steady-states are possible.

Next, the value of knowing the mapping from original system parameters to normal form parameters will be explored. In particular, the three-dimensional case (n=2) will be examined for ρ=2. The steady states in this case are

$$x_{1s}\Big|_{1,2} = -\frac{1}{2}\frac{d_1d_2d_3}{db_2b_3} \pm \frac{1}{2}\sqrt{(d_1d_2d_3/db_2b_3)^2 + 4\theta\, d_1d_2d_3/db_2b_3} \tag{39}$$

Introducing new variables which translate the normal form variables so that zero is a steady state,

$$\begin{aligned} z_1 &= x_1 - x_{1s}\Big|_2 \\ z_2 &= x_2 \\ z_3 &= x_3 \ . \end{aligned} \tag{40}$$

[$x_{1s}\Big|_2$ denotes the steady state taking the minus sign in Eqn. (39)], system (33) becomes:

$$\begin{aligned} \dot{z}_1 &= z_2 \\ \dot{z}_2 &= z_3 \end{aligned}$$

$$\dot{z}_3 = d^2b_2^2b_3^2z_1^2 - \sqrt{(d_1d_2d_3)^2 + 4\theta\, d_1d_2d_3db_2b_3}\, z_1 - (d_1d_2 + d_1d_3 + d_2d_3)z_2 + (d_1 + d_2 + d_3)z_3 \,. \tag{41}$$

From Eqn. (41) it is very easy to find, for example, conditions to be satisfied for the system to Hopf bifurcate to periodic solutions. Making use of Eqn. (8), the characteristic equation is

$$s^3 - (d_1 + d_2 + d_3)s^2 + (d_1d_2 + d_1d_3 + d_2d_3)s + \sqrt{(d_1d_2d_3)^2 + 4\theta\, d_1d_2d_3db_2b_3} = 0 \,. \tag{42}$$

Using then the approach suggested in [1], the following explicit conditions in terms of the system parameters for Hopf bifurcation are obtained:

$$d_1d_2 + d_1d_3 + d_2d_3 > 0 \tag{43.1}$$

and

$$\sqrt{(d_1d_2d_3)^2 + 4\theta\, d_1d_2d_3db_2b_3} = -(d_1 + d_2 + d_3)(d_1d_2 + d_1d_3 + d_2d_3) \,. \tag{43.2}$$

Similarly, one can also identify conditions for higher order bifurcations [1].

Normal forms may be extremely useful for establishing relationships between different models which, although apparently different in their original formulation, have identical normal forms. For example, the companion normal form for the model considered here [Eqn. (41)] is identical in structure to another model which is known to display complicated nonlinear oscillations. This model was presented previously [9] in the form

$$\begin{aligned} \dot{p} &= -q - r \\ \dot{q} &= p \\ \dot{r} &= \gamma(q - q^2) - \delta r \,. \end{aligned} \tag{44}$$

The solutions of these equations, for certain values of the parameters γ and δ, exhibit toroidal oscillations [9] which arise from an F_2 bifurcation involving a zero eigenvalue and a conjugate imaginary pair of eigenvalues. Bifurcation occurs for $\gamma > 0$ and $\delta = 0$, and toroidal oscillations are evident for, e.g. $\gamma = 0.375$ and $\delta = 0.23$. System (42)

may be converted to the companion normal form by affine transformation to obtain

$$\frac{d\hat{p}}{dt} = \hat{q}$$

$$\frac{d\hat{q}}{dt} = \hat{r} \tag{45}$$

$$\frac{d\hat{r}}{dt} = \gamma\hat{p}^2 - (\gamma + \delta)\hat{p} - \hat{q} - \delta\hat{r} \ .$$

This equation has identical form to Eqn. (41). Equating coefficients of corresponding terms in the final equations in both sets gives the following relationships among the parameters of the two models:

$$d^2b_2^2b_3^2 = \gamma$$

$$(d_1d_2d_3)^2 + 4\theta d_1d_2d_3db_2b_3 = \gamma + \delta \tag{46}$$

$$d_1d_2 + d_1d_3 + d_2d_3 = 1$$

$$d_1 + d_2 + d_3 = -\delta$$

or

$$d_1d_2d_3 = \mp 2\sqrt{\gamma}\,\theta \pm \sqrt{4\gamma\theta^2 - (\gamma + \delta)}$$

$$d_1d_2 + d_1d_3 + d_2d_3 = 1 \tag{47}$$

$$d_1 + d_2 + d_3 = -\delta \ .$$

For certain values of γ and δ, system (47) has a solution for the d_i's if and only if for some value of θ the polynomial

$$s^3 + \delta s^2 + s + (\pm 2\sqrt{\gamma}\,\theta \pm \sqrt{4\gamma\theta^2 - (\gamma + \delta)} = 0 \tag{48}$$

has three real roots. The condition that this be true is [10]:

$$4\left[1 - \frac{\delta^2}{3}\right]^3 + \left[-\frac{2\delta^3}{27} + \frac{\delta}{3} \pm 2\sqrt{\gamma}\,\theta \pm \sqrt{4\gamma\theta^2 - (\gamma + \delta)}\right]^2 < 0 \ . \tag{49}$$

Interestingly, this condition is not satisfied for $\gamma = 0.375$ and $\delta = 0.23$, values for which model (44) is known to exhibit toroidal oscillations. This means that, although system (44) is of the same functional form as (41), the two systems are not equivalent for all values of their system parameters. Establishment of the correspondence between system and normal form parameters allows this conclusion to be made. For γ and δ values satisfying condition (49), the two different models are totally equivalent.

NORMAL FORMS OF F_1 AND G_1 BIFURCATIONS: COINCIDENCE WITH COMPANION NORMAL FORMS FOR TWO- AND THREE-DIMENSIONAL SYSTEMS

Consider an n-dimensional dynamic system of the form:

$$\dot{w} = \hat{f}(w,\nu) \tag{50}$$

In a previous publication [1] it was seen that variation of two system parameters can realize an F_1 bifurcational structure. That is, the Jacobian of system (50), when converted to its Jordan normal form, has a Jordan block of the form

$$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \tag{51}$$

The normal form in this case is [11]

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = f_1(\hat{x}_1,\varepsilon_1,\varepsilon_2) + f_2(\hat{x}_1)\hat{x}_2 \tag{52}$$

Bogdanov [11] and others have examined in detail such normal forms. These studies reveal that 32 different phase portraits involving two or three steady states can arise as the parameters ε_1 and ε_2 are varied. Letting more parameters vary, one can obtain higher order bifurcational structures. For three-parameter variation, the highest order bifurcation that can arise is G_1 and the corresponding normal form is [12]:

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = \hat{x}_3$$

$$\frac{d\hat{x}_3}{dt} = f_1(\hat{x}_1) + f_2(\hat{x}_1)\hat{x}_2 + f_3(\hat{x}_1,\hat{x}_2,\hat{x}_3)\hat{x}_3 \tag{53}$$

It is immediately apparent that Eqns. (52) and (53) are in the companion normal form. Consequently, the classical normal form obtained from considerations of the Jordan block structure for F_1 and G_1 bifurcations coincides with the companion normal form for two- and three-dimensional systems, respectively. As a result, reducing two- and three-dimensional systems by affine transformation to the companion normal form also gives the classical normal form. Two- and three-dimensional systems so transformable to the companion normal form may therefore be considered as F_1 and G_1 systems, respectively, and the body of theory and experience developed for those cases may be applied.

The highest order bifurcational structure that can be stabilized for a two-dimensional system is the F_1 bifurcation. The codimension of a certain structure (steady state and eigenvalue) is defined as the minimum number of independent parameters needed to realize this structure. Consider a two-dimensional system which is reduced via affine transformation to the form of Eqn. (52). The Jacobian at a steady state $(\hat{x}_{1s},\hat{x}_{2s})$ is given by

$$\begin{bmatrix} 0 & 1 \\ f'_1(\hat{x}_{1s}) & f_2(\hat{x}_{1s}) \end{bmatrix}, \tag{54}$$

and the steady states are solutions of the equation

$$f_1(\hat{x}_{1s}) = 0 \ . \tag{55}$$

Necessary conditions for an F_1 bifurcation are that, at the steady state $\hat{x}_{1s}$, the following are true:

$$f_1(\hat{x}_{1s}) = f'_1(\hat{x}_{1s}) = f_2(\hat{x}_{1s}) = 0 \,. \tag{56}$$

These three equations have as unknowns $\hat{x}_{1s}$ *and system parameters. Typically, two* system parameters will require adjustment to specific values to satisfy conditions (56).

If, however, the conditions

$$f_1''(\hat{x}_{1s}) = f_1^{(3)}(\hat{x}_{1s}) = \cdots f_1^{(\bar{r})}(\hat{x}_{1s}) = 0,\ f_1^{(\bar{r}+1)}(\hat{x}_{1s}) \neq 0, \tag{57}$$

are enforced in addition, a higher codimension F_1 bifurcation is effected. The function $f_1(\hat{x}_1)$ is then contact equivalent to the germ [7,8]

$$u^{\bar{r}+1} - \lambda \tag{58}$$

with unfolding:

$$u^{\bar{r}+1} - a_{\bar{r}-1}u^{\bar{r}-1} - a_{\bar{r}-2}u^{\bar{r}-2} - \cdots - a_1 u - \lambda = 0 \,. \tag{59}$$

It is evident that to achieve this higher order contact at the F_1 point, one usually needs to adjust $\bar{r} + 1$ parameters. Then this is F_1 bifurcation of co-dimension $(\bar{r} + 1)$.

Consider the codimension-2 F_1 bifurcation case (only Eqns. (56) are satisfied). The function $f_1(x)$ in this case is contact equivalent to the germ u^2. This system is equivalent to

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = \hat{x}_1^2 - a_1\hat{x}_1 - a_2 + f_2(\hat{x}_1, a_1, a_2)\hat{x}_2 \,;$$

$$f_2(0,0,0) = 0 \tag{60}$$

The steady states of system (60) are:

$$\hat{x}_{1s} = \frac{a_1 \pm \sqrt{a_1^2 + 4a_2}}{2} \tag{61}$$

and are zero, one or two in number depending on a_1 and a_2. The eigenvalues of the Jacobian are then

$$S_{\pm} = \frac{f_2(\hat{x}_{1s}, a_1, a_2) \pm \sqrt{f_2^2(\hat{x}_{1s}, a_1, a_2) \pm 4\sqrt{a_1^2 + 4a_2}}}{2}. \tag{62}$$

In the case of two steady states, one is easily seen to be a saddle. The other steady state, depending on the value of f_2, can have any of the eigenvalue configurations sketched in Fig. 1.

If in addition the condition $f_1''(\hat{x}_{1s}) = 0$ is enforced, codimension three F_1 bifurcation results. Three steady states are involved, and, according to Eqn. (59), the unfolding is

$$u^3 - a_2 u - a_3 \tag{63}$$

involving two parameters. The eigenvalue structure, however, depends on one additional parameter and for this reason the unfolding that must be considered is

$$u^3 - a_1 u^2 - a_2 u - a_3 \ . \tag{64}$$

giving rise to an equivalent system of the form

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = \hat{x}_1^3 - a_1\hat{x}_1^2 - a_2\hat{x}_1 - a_3 + f_2(\hat{x}, a_1, a_2, a_3)\hat{x}_2 \tag{65}$$

Again, the steady states may be found as functions of the parameters a_1, a_2 and a_3 and the eigenvalues of the Jacobian may be computed.

In the case of feedback-induced bifurcation [16], there is a reference steady state which is unaffected by control gain parameters. As a result the system is equivalent to

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = h(\hat{x}_1)\hat{x}_1 - \hat{g}(\hat{x}_1)\hat{x}_2 \tag{66a}$$

with steady states (0,0) and others that correspond to $h(\hat{x}_1) = 0$. In this case the simplest possibility is that system is equivalent to

$$\frac{d\hat{x}_1}{dt} = \hat{x}_2$$

$$\frac{d\hat{x}_2}{dt} = \hat{x}_1^2 - a_1\hat{x}_1 - \hat{g}_2(\hat{x}_1, a_1, a_2)\cdot\hat{x}_2 \tag{66b}$$

In addition to (0,0) there is a steady state $(a_1,0)$. Again, on perturbation, one steady state is a saddle, and the other has one of the four possible eigenvalue configurations shown in Fig. 1. Higher order contacts may be treated similarly.

A CHEMICAL TWO-DIMENSIONAL F_1 SYSTEM

Consider the catalytic reaction

$$2A + B \rightarrow 2C \tag{67}$$

and assume that it proceeds via the following elementary steps:

$$A + X \Leftrightarrow AX \tag{68.1}$$

$$B + 2X \Leftrightarrow BX_2 \tag{68.2}$$

$$B + X \Leftrightarrow BX \tag{68.3}$$

$$2AX + BX_2 \rightarrow 2C + 4X \tag{68.4}$$

Making the assumptions that B reacts via a chemisorbed BX_2 which is available only at very low concentration, that mass action kinetics apply, and that the gas species concentrations [A] and [B] are fixed, Eigenberger [4] arrived at the following mathematical model:

$$\frac{d\tilde{y}_1'}{dt} = \tilde{\kappa}_1[A](\tilde{y}_2' - \tilde{y}_1') - \tilde{\kappa}_{-1}\tilde{y}_1' - 2\tilde{\kappa}_3[B]\tilde{y}_1'^2(\tilde{y}_1' - \tilde{y}_2')^2 \tag{69.1}$$

$$\frac{d\tilde{y}_2'}{dt} = -\tilde{\kappa}_3[B](\tilde{y}_2' - \tilde{y}_1') + \tilde{\kappa}_{-3}(1 - \tilde{y}_2') \tag{69.2}$$

where $\tilde{y}_1' = [AX]$, $\tilde{y}_2' = 1 - [BX]$, and the mass balance $[AX] + [BX] + [X] = 1$ has been invoked. System (69) for different values of the system parameters gives rise to

steady-state multiplicity, relaxation oscillations involving three steady states, and harmonic oscillations [4]. All these phenomena are typical of an F_1 system [3] and hence in what follows system (69) is treated as such. Introducing dimensionless quantities the system model may be reduced to the form of system (11) with

$$\mathbb{K} = \begin{bmatrix} -(\hat{a}_1 + \hat{a}_2) & \hat{a}_1 \\ \hat{a}_3 & -(\hat{a}_3 + \hat{a}_4) \end{bmatrix}$$

$$\mathbf{A} = [-1 \quad 0]^T, \quad h(\bar{y}) = \bar{y}_1^2(\bar{y}_1 - \bar{y}_2)^2$$

and

$$\mathbf{m} = [0 \quad \hat{a}_4]^T. \tag{70}$$

From Eqn. (13)

$$\mathbf{S}^{-1} = \begin{bmatrix} \hat{f}_1 & \hat{f}_2 \\ -(\hat{a}_1 + \hat{a}_2)\hat{f}_1 + \hat{a}_3\hat{f}_2 & \hat{a}_1\hat{f}_1 - (\hat{a}_3 + \hat{a}_4)\hat{f}_2 \end{bmatrix}. \tag{71}$$

Further from Eqn. (14)

$$\mathbf{S}^{-1}\mathbf{A} = \hat{\mathbf{b}} \Rightarrow \begin{bmatrix} -\hat{f}_1 \\ (\hat{a}_1 + \hat{a}_2)\hat{f}_1 - \hat{a}_3\hat{f}_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \tag{72}$$

From this, one obtains

$$\hat{f}_1 = 0; \quad \hat{f}_2 = -\frac{1}{\hat{a}_3}. \tag{73}$$

Using Eqns. (73), (71) becomes

$$\mathbf{S}^{-1} = \begin{bmatrix} 0 & \frac{1}{\hat{a}_3} \\ -1 & \frac{\hat{a}_3 + \hat{a}_4}{\hat{a}_3} \end{bmatrix}. \tag{74}$$

Now,

$$\mathbb{K}^{-1} = \begin{bmatrix} -(\hat{a}_3 + \hat{a}_4) & -\hat{a}_1 \\ -\hat{a}_3 & -(\hat{a}_1 + \hat{a}_2) \end{bmatrix} \cdot \frac{1}{\hat{a}_2\hat{a}_3 + \hat{a}_2\hat{a}_4 + \hat{a}_1\hat{a}_4}.$$

(75)

Consequently,

$$S^{-1}K^{-1}m = \begin{bmatrix} \dfrac{(\hat{a}_1 + \hat{a}_2)\hat{a}_4}{\hat{a}_3(\hat{a}_2\hat{a}_3 + \hat{a}_2\hat{a}_4 + \hat{a}_1\hat{a}_4)} \\ \dfrac{-\hat{a}_4}{\hat{a}_3} \end{bmatrix}. \tag{76}$$

and, as a result, the required affine transformation to bring the system to the companion normal form is the following

$$\begin{aligned} \tilde{x}_1 &= -\frac{\tilde{y}_2'}{\hat{a}_3} + \frac{(\hat{a}_1 + \hat{a}_2)\hat{a}_4}{\hat{a}_3(\hat{a}_2\hat{a}_3 + \hat{a}_2\hat{a}_4 + \hat{a}_1\hat{a}_4)} \\ \tilde{x}_2 &= -\tilde{y}_1' + \frac{\hat{a}_3 + \hat{a}_4}{\hat{a}_3}\tilde{y}_2' - \frac{\hat{a}_4}{\hat{a}_3}. \end{aligned} \tag{77}$$

One can then compute

$$A = S^{-1}KS = \begin{bmatrix} 0 & 1 \\ -(\hat{a}_1\hat{a}_4 + \hat{a}_2\hat{a}_3 + \hat{a}_3\hat{a}_4) & -(\hat{a}_1 + \hat{a}_2 + \hat{a}_3 + \hat{a}_4) \end{bmatrix} \tag{78}$$

and

$$\begin{aligned} f(\cdot) = \tilde{y}_1'^2(\tilde{y}_1' - \tilde{y}_2')^2 &= \left[-(\hat{a}_3 + \hat{a}_4)\tilde{x}_1 - \tilde{x}_2 + \frac{\hat{a}_1\hat{a}_4}{\hat{a}_2\hat{a}_3 + \hat{a}_2\hat{a}_4 + \hat{a}_1\hat{a}_4} \right]^2 \cdot \\ &\times \left[-\hat{a}_4\tilde{x}_1 - \tilde{x}_2 - \frac{\hat{a}_2\hat{a}_4}{\hat{a}_2\hat{a}_3 + \hat{a}_2\hat{a}_4 + \hat{a}_1\hat{a}_4} \right]^2 . \end{aligned} \tag{79}$$

After some manipulation, the transformed system becomes

$$\frac{d\tilde{x}_1}{dt} = \tilde{x}_2$$

$$\begin{aligned} \frac{d\tilde{x}_2}{dt} = &\{ h_{11}(\hat{a}_3,\hat{a}_4)x_1^4 + h_{12}(\hat{a})x_1^3 + h_{13}(\hat{a})x_1^2 + h_{14}(\hat{a})x_1 + h_{15}(\hat{a}) \} \\ &+ \tilde{x}_2 \{ h_{21}(\hat{a}_3,\hat{a}_4)x_1^3 + h_{22}(\hat{a})x_1^2 + h_{23}(\hat{a})x_1 + h_{24}(\hat{a}) \} \end{aligned}$$

$$+ \bar{x}_2^2 \{ h_{31}(\hat{a}_3,\hat{a}_4)x_1^2 + h_{32}(\hat{a})x_1 + h_{33}(\hat{a}) \} + \bar{x}_2^3 \{ h_{41}(\hat{a}_3,\hat{a}_4)x_1 + h_{42}(\hat{a}) \} + \bar{x}_2^4 \ . \tag{80}$$

All of the hij with the exception of the h_{i1} are functions of all system parameters $\hat{a}_1$ to $\hat{a}_4$.

System (80) has the same steady-state and eigenvalue structure as the system

$$\frac{d\bar{x}_1}{dt} = \bar{x}_2$$

$$\frac{d\bar{x}_2}{dt} = \{ h_{11}\bar{x}_1^4 + h_{12}\bar{x}_1^3 + h_{13}\bar{x}_1^2 + h_{14}\bar{x}_1 + h_{15} \} + \bar{x}_2 \{ h_{21}\bar{x}_1^3 + h_{22}\bar{x}_1^2 + h_{23}\bar{x}_1 + h_{24} \} \tag{81}$$

From the form of Eqn. (81), one can see that the system has a maximum of four steady states. Indeed, four steady states were observed for some parameter values by Eigenberger, one of which was not in the positive orthant.

Varying different parameters, this system may be brought to F_1 bifurcation of different codimensions. Conditions for different cases are listed next:

i. **Codimension-2 F_1 Bifurcation:**

Necessary conditions are:

$$\begin{aligned} h_{11}\bar{x}_1^4 + h_{12}\bar{x}_1^3 + h_{13}\bar{x}_1^2 + h_{14}\bar{x}_1 + h_{15} &= 0 \\ 4h_{11}\bar{x}_1^3 + 3h_{12}\bar{x}_1^2 + 2h_{13}\bar{x}_1 + h_{14} &= 0 \\ h_{21}\bar{x}_1^3 + h_{22}\bar{x}_1^2 + h_{23}\bar{x}_1 + h_{24} &= 0 \end{aligned} \tag{82}$$

Clearly, variation of two system parameters may realize this structure. On perturbing from the F_1 bifurcation point there are two nearby steady states.

ii. **Codimension-3 F_1 Bifurcation:**

All of conditions (82) must be satisfied and in addition:

$$6h_{11}\bar{x}_1^2 + 3h_{12}\bar{x}_1 + h_{13} = 0 \tag{83}$$

Solving Eqn. (83) for $\bar{x}_1$ and substituting in Eqn. (82), one obtains three equations

to be satisfied by parameters $\hat{a}_1$ to $\hat{a}_4$. Thus, adjustment of three parameters is required.

iii. **Codimension-4 F_1 Bifurcation:**

In addition to conditions (82) and (83), the following equation must be satisfied:

$$4h_{11}\tilde{x}_1 + h_{12} = 0 \tag{84}$$

Solving Eqn. (4) for $\tilde{x}_1$ and substituting in Eqns. (82) and (83), one obtains:

$$\begin{gathered} 256h_{11}^3h_{15} - h_{12}^4 = 0 \\ 16h_{11}^2h_{14} - h_{12}^3 = 0 \\ 8h_{11}h_{13} - 3h_{12}^2 = 0 \\ -\frac{h_{21}h_{12}^3}{64h_{11}^3} + \frac{h_{22}h_{12}^2}{16h_{11}^2} - \frac{h_{23}h_{12}}{4h_{11}} + h_{24} = 0 \end{gathered} \tag{85}$$

which must all be satisfied by $\hat{a}_1$ through $\hat{a}_4$ for this highest possible codimension F_1 bifurcation for this system. At this point in the four-dimensional parameter space, the function $h_{11}\tilde{x}_1^4 + \ldots + h_{15}$ is contact equivalent to the germ $\tilde{x}_1^4 - \lambda$. A small perturbation in the proper direction may give rise to four steady states, whereas at exactly the codimension-4 F_1 bifurcation point all four steady states coincide. As a consequence, by studying the local properties of the system on perturbing from this highest order bifurcation point, one can discover all the possible steady-state and eigenvalue configurations.

CONCLUSIONS

The normal form of a dynamic system is a much simpler set of equations that retains all of the important local dynamic features of the original system. In general it is very hard to transform a system to the corresponding normal form and to deduce from that possible dynamic behavior. Systems with a single nonlinearity

are shown here to be reducible by affine transformation to the so-called companion normal form that has distinct advantages. One can deduce what steady-state bifurcations and eigenvalue structures are possible. In the cases of two- and three-dimensional systems, the companion normal form coincides with the classical F_1 and G_1 bifurcation normal forms, respectively, that are based on Jordan block structure.

For a generalized enzymatic feedback system, the transformation to the companion normal form has been executed, and the much simpler system reveals which groupings of original system parameters can be varied independently to influence the system steady-state and dynamic properties. Different codimension F_1 bifurcations were identified for two-dimensional systems. A chemical example was shown to exhibit a codimension-4 F_1 bifurcation as its highest order bifurcational structure.

Acknowledgment

This work was supported by the National Science Foundation.

Nomenclature

A,B,C:	Chemical species in second example.
AX, BX, BX_2:	Chemical species in second example.
a_i:	Parameters in Eqn. (58).
$\mathbf{A}$:	Matrix in Eqn. (1).
$\hat{b}, \hat{c}$:	Vectors in Eqn. (1).
$\tilde{b}$:	Vector, see Eqn. (23).
b_i, c_i, d_i:	Eqn. (24).
$\hat{d}$:	Constant in Eqn. (4).
d:	αb_e.
E_i:	Enzyme concentrations.
$E_i(0)$:	See Eqn. (23).
f:	Function in Eqn. (1).
$\tilde{f}$:	Vector in Eqn. (13).
$\hat{f}$:	Function in Eqn. (50).
$\hat{f}_1, \hat{f}_2$:	See Eqn. (71).
f_1, f_2, f_3:	Functions in normal forms (52), (53).
$\mathbf{g}$	Constant vector in Eqn. (9).
h:	Function defined in (26.2).
H_i:	Bimolecular rate constants.
h_i:	Unimolecular rate constant for dissociation of X_i to S_i and E_i.

h_{ij}: Function of $\hat{\alpha}$ in Eqn. (80).

j_i, j_{-i}: Rate constants for exchange of substrates S_i.

J: Jacobian matrix in Eqn. (54).

K: Matrix defined in Eqn. (12).

$\tilde{k}$: Constants in Eqn. (69).

${}^iK_m$: Defined in Eqn. (23).

m: Vector in Eqn. (12).

n: Dimensionality of system (1).

p,q,r: Variables in Eqn. (44).

$\hat{p},\hat{q},\hat{r}$: Variables in Eqn. (45).

$\tilde{r}$: Power in Eqn. (57).

s: Variable in Eqn. (8).

S: Matrix in Eqn. (9).

s_{ij}: Entries of matrix S.

S_i: Substrates' concentrations.

u: Unfolding variable, see Eqn. (59).

${}^iV_m$: Defined in Eqn. (23).

w: Variables in system (23).

X_i: Enzyme-substrate complexes concentration.

X: Surface site in second example.

ξ: State vector in normal forms (52) and (53).

$\tilde{\mathbf{x}}$ Defined in Eqn. (77).

$\mathbf{x}$ State vector in system (1).

$x_{i\infty}$: Steady-state values of x_i.

$\mathbf{y}$: State vector in Eqn. (9).

$y_1,\ldots,y_{n+1}$: See Eqn. (24).

$\tilde{y}_1'$: [AX].

$\tilde{y}_2'$: 1 - [EX].

$\tilde{y}_1,\tilde{y}_2$: Dimensionless concentrations in second example.

$\tilde{z}$: Introduced in Eqn. (36).

$\mathbf{z}$ State vector introduced in Eqn. (40).

GREEK SYMBOLS

α_0: Defined in Eqn. (37).

α: H_{n+1}/h_{n+1}.

α_i: Defined in Eqn. (24).

$\hat{\alpha}_i$: Dimensionless rate constants in second example.

γ, δ: Parameters in system (44).

$\varepsilon_1, \varepsilon_2$: Parameters in normal form (52).

θ: Defined after Eqn. (31).

κ: $H_0 S_0$.

κ_i: Rate constants in first example.

λ: See Eqn. (58).

Λ: Vector defined in Eqn. (12)

ρ: Exponent in Eqn. (20).

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Figure Captions

Figure 1: Sketch of different possible eigenvalue configurations at the second steady state for codimension-2 F_1 bifurcation and feedback-induced F_1 bifurcation of a two-dimensional system.

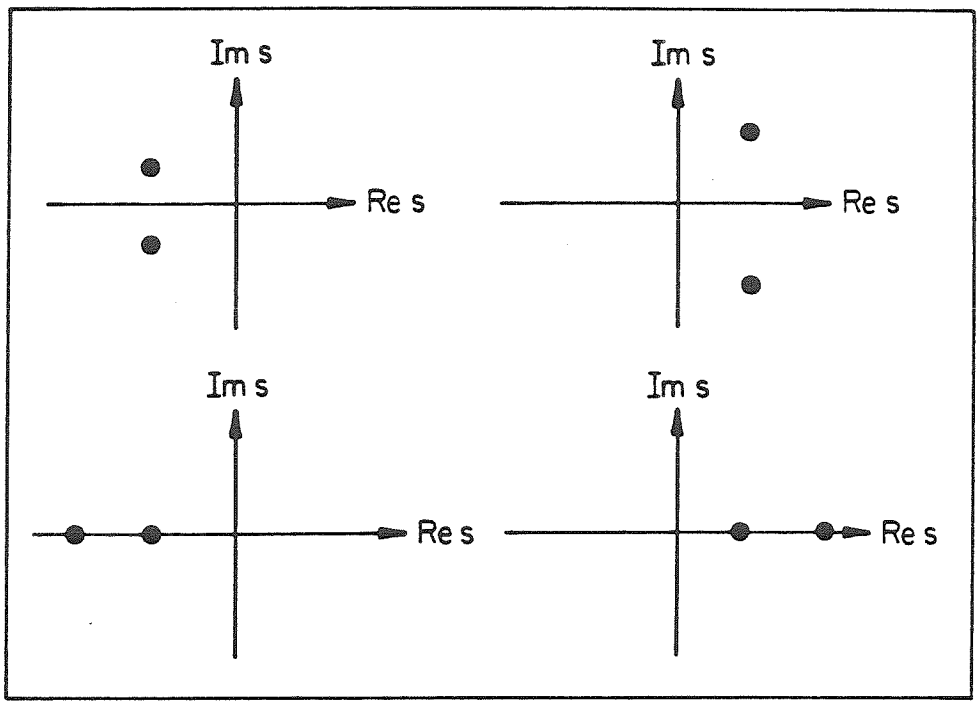

FIGURE 1

CHAPTER 6 : BIFURCATIONS FROM THE POTENTIAL FIELD ANALOG OF SOME CHEMICAL REACTION SYSTEMS

INTRODUCTION

In a previous publication [1], the value of normal forms in describing the different possible dynamic properties of lumped chemical systems was demonstrated. In general, a nonlinear transformation is involved in bringing a dynamic system to its normal form [1,2]. Although, in principle, finding the required nonlinear transformation is a mathematically involved process, a certain class of systems may be reduced by an affine transformation to the so-called companion normal form which clearly retains the steady state and dynamic characteristics of the original system [3]. Having this form it is easy to obtain the dependence of the steady-state and eigenvalue structure on the original system parameters.

For the cases of two- and three-dimensional systems, which are reducible to this form, the companion normal form coincides with the normal forms of F_1 and G_1 bifurcation, respectively [3]. These types of bifurcation consist of two and three real eigenvalues crossing simultaneously the imaginary axis and are the highest order bifurcations possible for two- and three-dimensional systems, respectively.

The normal form of a system close to a G_1 bifurcation has the structure [4]:

$$\begin{aligned} \dot{x} &= y \\ \dot{y} &= z \\ \dot{z} &= f_1(x) + f_2(x)y + f_3(x,y,z)z \end{aligned} \tag{1}$$

If it happens that the function $f_3(x,y,z)$ is a negative constant, system (1) has a constant negative divergence. The concept of a potential function may then be introduced to gain special insights into the system dynamics and to derive conclusions regarding global stability characteristics of the system in question.

In the subsequent section the theory for systems of constant negative divergence reducible to the form of system (1) is developed. The results are then applied to a class of enzymatic reaction systems.

BIFURCATIONS FROM THE POTENTIAL WELL

Consider a system which is reducible by an affine transformation of the form

$$y = Ax + g \tag{2}$$

to a system

$$\begin{aligned} \dot{x} &= y \\ \dot{y} &= z \\ \dot{z} &= f(x) + \alpha(x)y - bz \end{aligned} \tag{3}$$

System (3) may be written in the form

$$\begin{aligned} \ddot{x} &= z \\ \dot{z} &= f(x) + \alpha(x)\dot{x} - bz \ . \end{aligned} \tag{4}$$

It will be shown next that as $b \to \infty$, system (4) essentially reduces to a two-dimensional system that may be viewed as describing the motion of a particle in a potential well. This analogy provides special insight and easy analysis of the dynamics of (3) even for $b > 0$, but finite since results regarding local stability are obtained in this case.

Rearranging the second equation of system (4) gives

$$\dot{z} + bz = f(x) + \alpha(x)\dot{x} \ . \tag{5}$$

Writing the analytical solution for z in Eqn. (5) and noting that

$$\int_0^t \alpha(x(\tau))\dot{x}(\tau)e^{b\tau}d\tau = A(x(t))e^{bt} - A(x_0) - \int_0^t bA(x(\tau))e^{b\tau}d\tau$$

(6)

where

$$A(x) \triangleq \int_0^x a(s)ds \,, \tag{7}$$

there results

$$z = z_0 e^{-bt} + A(x - A(x_0)e^{-bt} + \int_0^t [f(x(t-\tau)) - bA(x(t-\tau))]e^{-b\tau}d\tau \,. \tag{8}$$

The integral in the RHS of Eqn. (8) belongs to a class of integrals called Laplace integrals [5,6]. In the limit as $b \to +\infty$, Watson's lemma [5,6] provides the full asymptotic expansion of the integral. Expanding the function in the integral in a Taylor series, one obtains the leading terms

$$f(x(t-\tau)) - bA(x(t-\tau))] \approx [f(x(t)) - bA(x(t))]$$

$$-[f'(x(t)) - bA'(x(t))]\dot{x}(t)\tau + 0(\tau^2) \,. \tag{9}$$

Application of Watson's lemma and using the first two terms of the RHS of Eqn. (9) gives immediately

$$\int_0^t [f(x(t-\tau)) - bA(x(t-\tau))]e^{-b\tau}d\tau \approx \frac{f(x) - bA(x)}{b} - \frac{[f'(x) - bA'(x)]\dot{x}}{b^2} \,. \tag{10}$$

Substituting this result in Eqn. (8) and noticing that for large t the terms z_0e^{-bt} and $A(x_0)e^{-bt}$ can be neglected, one obtains

$$z = \frac{f(x)}{b} - \frac{f'(x) - bA'(x)}{b^2}\dot{x} \,. \tag{11}$$

Recalling Eqn. (7), Eqn. (11) becomes

$$z = \frac{f(x)}{b} - \frac{f'(x) - ba(x)}{b^2}\dot{x} \,. \tag{12}$$

Finally, using Eqn. (12) in Eqn. (4), it is established that for sufficiently large b, System 2 is equivalent to

$$\ddot{x} + \frac{f'(x) - b\alpha(x)}{b^2}\dot{x} - \frac{f(x)}{b} = 0 \ . \tag{13}$$

Equation (13) may be viewed as describing the motion of a particle in a one-dimensional potential field, u(x), given by

$$\frac{du(x)}{dx} = -\frac{f(x)}{b} \ . \tag{14}$$

The function u(x) has turning points at the zeros of the function f(x), as is obvious from Eqn. (14). Letting x^* denote a zero of f(x), x^* gives a maximum in the potential function if $f'(x^*) > 0$. When $f'(x^*) < 0$, x^* is a minimum of u(x). When $f'(x^*) = 0$, one must check the higher order derivatives to arrive at any conclusion regarding the nature of the turning point. If $f''(x^*)$, or a higher even order derivative is different from zero, the turning point is a point of inflection (zero curvature).

The first derivative term in Eqn. (13) is equivalent to the "friction" or "damping" of the system. In general, the friction $[f'(x) - b\alpha(x)]/b^2$ is a function of x and acts to decelerate (if >0; positive friction) or accelerate (if <0; negative friction) the particle. If the friction vanishes for all values of x, the system is non-dissipative. In this case one expects, in general, the particle to oscillate indefinitely in a "valley" of the potential well or to go to infinity. Its exact behavior will depend on the initial conditions. Similarly, it is easy to predict the fate of the particle in the event that friction is constant. For example, for positive friction, starting at rest close to a minimum in a "valley" , the particle will eventually attain this minimum.

If the "friction" term is a function of x, it is much harder, in general, to predict the motion of the particle. In some instances, however, the conditions of a theorem due to Lie'nard [7] are met which permits conclusions regarding the existence and uniqueness of stable periodic solutions. Equation (13) is of the

form of a general class of equations called the Lienard equations, which have the following form:

$$\ddot{x} + \hat{f}(x)\dot{x} + \hat{g}(x) = 0 \ . \tag{15}$$

The following theorem holds.

Theorem [7]: Equation (15) has a unique stable periodic solution if $\hat{f}$ and $\hat{g}$ are continuous, and

i. $\hat{F}(x) = \int_0^x \hat{f}(a)da$ is an odd function.

ii. $\hat{F}(x)$ is zero only at $x = 0$, $x = \hat{a}$ and $x = -\hat{a}$ for some $\hat{a} \geq 0$.

iii. $\hat{F}(x) \to \infty$ as $x \to \infty$ monotonically for $x > a$.

iv. $\hat{g}(x)$ is an odd function and $\hat{g}(x) > 0$ for $x > 0$.

It should be emphasized that the conditions of the theorem are sufficient only. A system may possess stable periodic solutions even if these conditions are not met. If the conditions of the preceding theorem are not met, one can still clearly see the different possibilities only by considering the shape of the potential function. This provides a special intuition which one could not possibly have for the original system (3). All that is required is plotting u(x). Then it is clear that the "particle" will go to a minimum, oscillate in a "basin", perform an oscillatory motion in more than one "basin" (if applicable), or go to infinity.

Although the equivalence of systems (3) and (13) is clear for $b \to \infty$, the behavior of the dynamic system (13) may be shown also to be similar to that of system (3) locally; that is, close to a steady state for any $b > 0$. This will be demonstrated next.

As noted earlier, the steady states for both systems (3) and (13) are given by

$$f(x^*) = 0 \ . \tag{16}$$

Equivalence of local dynamics near x^* is examined by comparing the eigenvalue structure of the two model Jacobians evaluated at x^*. The eigenvalues of the two-dimensional system (13) are given by

$$S_\pm = \frac{1}{2}\left[\frac{b\alpha(x^*) - f'(x^*)}{b^2} \pm \sqrt{\left[\frac{b\alpha(x^*) - f'(x^*)}{b^2}\right]^2 + \frac{4f'(x^*)}{b}} \right]. \tag{17}$$

It is easy to reach certain conclusions regarding the stability of the dynamic system based on Eqn. (17). First, consider the case of a maximum. At a maximum where $f'(x^*) > 0$, clearly the two eigenvalues are real and have opposite signs. As a result, maxima of the potential function are unstable saddle points.

When $f'(x^*) > 0$, the steady state x^* of system (3) is unstable. The characteristic equation of the Jacobian of this system evaluated at the steady-state x^* is

$$s^3 + bs^2 - \alpha(x^*)s - f'(x^*) = 0 \ . \tag{18}$$

Using the Descartes rule of signs [8], one finds that Eqn. (18) always has a positive real root for $f'(x^*) > 0$. This is so for any $b > 0$. Consequently, a steady state of system (3) corresponding to a maximum of the potential function $u(x)$ is always unstable. This is, of course, in accordance with intuition.

Consider next the stability of a steady state corresponding to a minimum of the potential function. At a minimum where $f'(x^*) < 0$, examination of Eqn. (17) shows that two eigenvalues have the same sign. The minimum will be stable if

$$f'(x^*) - b\alpha(x^*) > 0 \tag{19.1}$$

and unstable if

$$f'(x^*) - b\alpha(x^*) < 0 \tag{19.2}$$

This is again in accordance with intuition, since condition (19.1) implies positive "friction" whereas Eqn. (19.2) corresponds to negative "friction". When "friction" vanishes the two system eigenvalues are imaginary conjugate. For negative "friction", the minimum becomes unstable (Hopf bifurcates), and stable or unstable periodic solutions appear.

The conditions for Hopf bifurcation of system (3) are found according to Ref. [1] to be

$$\alpha(x^{\blacksquare}) < 0 \ , \tag{20.1}$$

$$f'(x^{\blacksquare}) - b\alpha(x^{\blacksquare}) = 0 \tag{20.2}$$

The first condition is met automatically for a minimum and, consequently, is redundant. At the Hopf bifurcation point the eigenvalues of system (3) are $\pm i\sqrt{-\alpha(x^{\blacksquare})}$ and -b. The first two are identical to those of system (13) while the other is negative for any $b > 0$. Consequently, the fate of the trajectories of system (3) is locally the same as are those of system (13). As a result it suffices to meet condition (20.2) for Hopf bifurcation at a steady state corresponding to a minimum of the potential function; this has the mechanical analog of the "friction" becoming negative.

The stability of the Hopf-induced limit cycles is determined by calculating the characteristic exponent of the transition matrix right after bifurcation [9]. Hassard et al. [9] have developed formulas for the leading term of an asymptotic expansion of the characteristic exponent treating the deviation from the critical bifurcation point as the perturbation parameter. If this leading term is negative, the induced limit cycle is stable; otherwise it is unstable. Following their suggestions, the leading term for the characteristic exponent for system (13) is found, after some tedious calculations, to be

$$\beta_2 = \frac{[b\alpha''(x^*) - f''(x^*)]f''(x^*)}{8b^3\alpha^2(x^*)} + \frac{b\alpha''(x^*) - f'''(x^*)}{8b^2} . \tag{21}$$

For systems of the form (3), one may use explicitly Eqn. (21) to determine the stability of the Hopf-induced limit cycles.

Having analyzed completely the case of Hopf bifurcation, the other possible types of bifurcation are considered next. D_1 bifurcation occurs when a single real eigenvalue crosses the imaginary axis and is accompanied usually by steady-state bifurcation. From Eqn. (18) it is easy to see that D_1 bifurcation for system (3) occurs when

$$f'(x^*) = 0 \tag{22.1}$$

and

$$\alpha(x^*) < 0 \tag{22.2}$$

The second condition guarantees that the remaining two nonzero eigenvalues are negative. The conditions where D_1 bifurcation occurs are the same for system (13). Condition (22.1) may imply that the potential function possesses an inflection point at D_1 bifurcation. As noted earlier, this will be true if $f''(x^*) \neq 0$ or, in general, if the first nonvanishing derivative of f is an even order derivative.

The highest order bifurcation for two-dimensional systems is F_1 [1]. In this case there is a double zero eigenvalue with the Jordan block

$$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} . \tag{22}$$

From (18) it follows that at an F_1 bifurcation the conditions

$$f'(x^*) = \alpha(x^*) = 0 \tag{23}$$

must be met for system (3). The third eigenvalue is -b.

Conditions (23) should be met also for system (13) at an F_1 bifurcation point.

The mechanical interpretation in this case is having no friction at the point at which $f'(x^*) = 0$ (which may be an inflection point). Close to an F_1 bifurcation, one expects steady-state multiplicity and relaxation oscillations [1].

It has been shown earlier that system (3) is equivalent to system (13) as $b \to \infty$. The preceding analyses demonstrate local equivalence between the two systems for $b > 0$. All of the qualitative aspects of the original system (3) local dynamics are preserved in the reduction to Eqn. (13).

Finally, it should be noted that higher order bifurcations of system (3) involving three eigenvalues [1] imply $b = 0$. Close to such bifurcations, system (3) is not locally equivalent to Eqn. (13). The original system has zero divergence for $b = 0$; it is termed Hamiltonian and has constant energy [e.g. 10]. For b small, one may treat the system as a perturbed Hamiltonian system. For b negative, the system has everywhere constant positive divergence and trajectories will definitely diverge to infinity.

DYNAMICS OF AN ENZYMATIC REACTION SYSTEM

In [3], the dynamic system describing the evolution of an enzymatic reaction system with feedback allosteric regulation [11] was shown to be reducible by an affine transformation to the following companion normal form in the three-dimensional case

$$\dot{\hat{x}} = \hat{y}$$

$$\dot{\hat{y}} = \hat{z}$$

$$\dot{\hat{z}} = (-db_2b_3\hat{x} - \theta)^p + (d_1d_2d_3)\hat{x} - (d_1d_2 + d_1d_3 + d_2d_3)\hat{y} + (d_1 + d_2 + d_3)\hat{z} \quad . \tag{24}$$

Let

$$\varepsilon_1 = d_1d_2d_3, \varepsilon_2 = d_1d_2 + d_1d_3 + d_2d_3, \varepsilon_3 = d_1 + d_2 + d_3 . \tag{25}$$

Since all the d_i must be real, ε_1, ε_2 and ε_3 can vary arbitrarily as long as the polynomial

$$\gamma^3 - \varepsilon_3\gamma^2 + \varepsilon_2\gamma - \varepsilon_1 = 0 \tag{26}$$

has three real roots. The condition that this is true is [8]:

$$4\left(\varepsilon_2 - \frac{\varepsilon_3^2}{2}\right)^3 + 27\left(-\varepsilon_1 + \frac{\varepsilon_2\varepsilon_3}{3} - \frac{2\varepsilon_3^3}{27}\right)^2 < 0 . \tag{27}$$

System (24) is of the form of system (3) with

$$\begin{aligned} \hat{f}(\hat{x}) &= (-db_2b_3\hat{x} - \theta)^\rho + \varepsilon_1\hat{x} \\ \hat{a}(\hat{x}) &= -\varepsilon_3 \\ b &= -\varepsilon_3 . \end{aligned} \tag{28}$$

Consequently, as $\varepsilon_3 \to -\infty$, the system is reduced to

$$\ddot{\hat{x}} + \frac{-\rho db_2b_3(-db_2b_3\hat{x} - \theta)^{\rho-1} + \varepsilon_1 - \varepsilon_2\varepsilon_3}{\varepsilon_3^2}\dot{\hat{x}} + \frac{(-db_2b_3\hat{x} - \theta)^\rho + \varepsilon_1\hat{x}}{\varepsilon_3} = 0 . \tag{29}$$

Quadratic Case ($\rho = 2$)

In this case the system becomes:

$$\ddot{\hat{x}} + \frac{2d^2b_2^2b_3^2\hat{x} + 2db_2b_3\theta + \varepsilon_1 - \varepsilon_2\varepsilon_3}{\varepsilon_3^2}\dot{\hat{x}} + + \frac{d^2b_2^2b_3^2\hat{x}^2 + 2db_2b_3\theta\hat{x} + \theta^2 + \varepsilon_1\hat{x}}{\varepsilon_3} = 0 \tag{30.1}$$

with

$$\hat{f}(\hat{x}) = d^2b_2^2b_3^2\hat{x}^2 + 2db_2b_3\theta\hat{x} + \theta^2 + \varepsilon_1\hat{x} . \tag{30.2}$$

The steady state are the zeros of the last term. Solving for the steady states yields

$$\hat{x}_s|_{1,2} = \frac{-2\theta d b_2 b_3 - \varepsilon_1 \pm \sqrt{\varepsilon_1^2 + 4\theta d b_2 b_3 \varepsilon_1}}{2d^2 b_2^2 b_3^2} . \tag{31}$$

Clearly, the condition that the system possesses two steady states is

$$\Delta = \varepsilon_1^2 + 4\theta d b_2 b_3 \varepsilon_1 > 0 . \tag{32}$$

Making use of Eqn. (14), the potential function is

$$\hat{U}(\hat{x}) = \frac{d^2 b_2^2 b_3^2 \hat{x}^3}{3\varepsilon_3} + \frac{(2d b_2 b_3 \theta + \varepsilon_1)\hat{x}^2}{2\varepsilon_3} + \frac{\theta^2 \hat{x}}{\varepsilon_3} . \tag{33}$$

This potential function is sketched in Fig. 1 in the case $\Delta > 0$. There are turning points at $\hat{x}_{s1}$ and $\hat{x}_{s2}$. The first is a minimum since $\hat{U}''(\hat{x}_{s1}) > 0$ whereas the second is a maximum as $\hat{U}''(\hat{x}_{s2}) < 0$, as can be seen easily from Eqns. (31) and (33).

Consider first the case of D_1 bifurcation. This will occur for $\Delta = 0$, $\varepsilon_3 > 0$. At this point there is a single steady state which corresponds to an inflection point of the potential function as $\hat{f}' = 0$ and $\hat{f}'' \neq 0$. D_1 bifurcation may or may not be accompanied by steady-state bifurcation.

To analyze the $\theta \neq 0$ case, assume without loss of generality that ε_1 is treated as the bifurcation parameter. For $\theta \neq 0$, D_1 bifurcation will occur for $\varepsilon_1 = 0$ and for $\varepsilon_1 = -4\theta d b_2 b_3$ ($\Delta = 0$). The condition that the bifurcation is a "limit point" bifurcation [12] is that $\partial \hat{f} / \partial \varepsilon_1 \, (\hat{x}_s) \neq 0$ at the critical value of the bifurcation parameter [12]. This is seen easily to be true for both $\varepsilon_1 = 0$ and $\varepsilon_1 = -4\theta d b_2 b_3$. For ε_1 between 0 and $-4\theta d b_2 b_3$, there are no steady states. For ε_1 outside this interval, there are two steady states (see Fig. 2).

In the case $\theta = 0$, the steady states are 0 and $-\varepsilon_1 / d^2 b_2^2 b_3^2$. D_1 bifurcation occurs for $\varepsilon_1 = 0$, and, in this case, $\partial \hat{f} / \partial \varepsilon_1 \, (\hat{x}_s) = 0$ at $\varepsilon_1 = 0$. This implies steady-state bifurcation with exchange of stabilities. For $\varepsilon_1 < 0$, the zero steady state is stable and the other steady state is unstable. For $\varepsilon_1 > 0$, the situation is

reversed (see Fig. 2). Consequently, the parameter θ is causing imperfect bifurcation [13] or, as is commonly said, "breaks" bifurcation.

The structure of the potential function close to D_1 bifurcation is portrayed in Fig. 3 for $\theta = 0$ and for $\theta \neq 0$. It is clear that D_1 bifurcation is reflected by a change in the structure of the potential function. The imaginary "particle" in each case will go either to the minimum of the potential function (if one exists), oscillate close to it, or go to infinity. It is possible from the structure of the potential well that the final fate of the system trajectories depends upon the initial point and velocity.

In order to examine the possibility of periodic behavior close to a steady state, we must consider Hopf bifurcation. In each case no Hopf bifurcation is possible from the maximum $\hat{x}_{s2}$. As the "friction" vanishes at the minimum, however, Hopf bifurcation occurs at the steady state which corresponds to the minimum ($\hat{x}_{s1}$). The conditions for Hopf bifurcation for the system at hand are

$$\varepsilon_2 > 0 \tag{34.1}$$

and

$$2d^2b_2^2b_3^2\hat{x}_{s1} + 2db_2b_3\theta + \varepsilon_1 - \varepsilon_2\varepsilon_3 = 0 \ . \tag{34.2}$$

Making use of Eqn. (21), the leading term in the asymptotic expansion for the characteristic exponent is found to be

$$\hat{\beta}_2 = \frac{d^4b_2^4b_3^4}{2\varepsilon_3^3\varepsilon_2^2} < 0 \ , \tag{35}$$

since $\varepsilon_3 < 0$. This implies that the Hopf-induced limit cycles are stable. If the initial energy of the "particle" is not very large and it lies initially inside the "basin" around the minimum, stable oscillations are expected. If, however, the initial energy exceeds that which is required to bring the "particle" past the

maximum $\hat{x}_{s2}$, one expects the particle to go to infinity. Consequently, stable oscillations are expected for the original system as long as the initial point is sufficiently close to the steady-state $\hat{x}_{s1}$. Finally, the conditions for an F_1 bifurcation are

$$\varepsilon_2 = \Delta = 0 \, . \tag{36}$$

As in the D_1 case, F_1 bifurcation will be accompanied by steady-state bifurcation only if $\theta \neq 0$.

Cubic Case ($\rho = 3$, $\theta = 0$)

For simplicity, only the case $\theta = 0$ is considered. In this case the system becomes

$$\ddot{\hat{x}} + \frac{-3d^3b_2^3b_3^3x_1^2 + \varepsilon_1 - \varepsilon_2\varepsilon_3}{\varepsilon_3^2}\dot{\hat{x}}$$

$$+ \frac{\varepsilon_1\hat{x} - d^3b_2^3b_3^3\hat{x}^3}{\varepsilon_3} = 0 \, . \tag{37}$$

Here,

$$\hat{f}(\hat{x}) = \varepsilon_1\hat{x} - d^3b_2^3b_3^3\hat{x}^3 \, . \tag{37.1}$$

If $\varepsilon_1 d b_2 b_3 > 0$, the system possesses three steady states:

$$\hat{x}_{s1} = 0 \, , \, \hat{x}_{s2} = -\sqrt{\frac{\varepsilon_1}{d^3b_2^3b_3^3}} \, , \, \hat{x}_{s3} = \sqrt{\frac{\varepsilon_1}{d^3b_2^3b_3^3}} \, . \tag{38}$$

Otherwise, zero is the only steady state. The potential function in this case is

$$\hat{U}(\hat{x}) = \frac{\varepsilon_1\hat{x}^2}{2\varepsilon_3} - \frac{d^3b_2^3b_3^3\hat{x}^4}{\varepsilon_3} \, . \tag{39}$$

Evaluating the second derivative of the potential function, it follows that nonzero steady states correspond to minima of the potential function if $\varepsilon_1 > 0$ and maxima if $\varepsilon_1 < 0$. All possible shapes of the potential function are shown in

Fig. 4 together with the cases of D_1 bifurcation. Again the shape of the potential function changes as D_1 bifurcation occurs. However, since $f''(\hat{x}_2) = 0$, the turning point at D_1 bifurcation is not an inflection point in this case.

Hopf bifurcations to periodic solutions are possible at the minima of the potential function in each case. The conditions for Hopf bifurcation are:

$$\varepsilon_2 > 0 \tag{40.1}$$

$$-3d^3b_2^3b_3^3\hat{x}^2 + \varepsilon_1 - \varepsilon_2\varepsilon_3 = 0 \ . \tag{40.2}$$

Consider each case in turn:

Case 1 ($db_2b_3 > 0$, $\varepsilon_1 < 0$):

Hopf bifurcation is possible at the minimum $\hat{x}_{s1} = 0$. Using Eqn. (21),

$$\hat{\beta}_2 = \frac{6d^3b_2^3b_3^3}{8b^3} > 0 \ . \tag{41}$$

Consequently in this case no stable periodic solutions are expected.

Case 2 ($db_2b_3 > 0$, $\varepsilon_1 > 0$):

Hopf bifurcation is possible only at the minima $\hat{x}_{s2}$ and $\hat{x}_{s3}$. In this case,

$$\hat{\beta}_2 = \frac{36\varepsilon_1 d^3b_2^3b_3^3}{8\varepsilon_3^3\alpha^2} + \frac{6d^3b_2^3b_3^3}{8\varepsilon_3^2} \ . \tag{42}$$

For $\beta_2 < 0$, the following inequality must hold:

$$6\varepsilon_1 + \varepsilon_3\varepsilon_2^2 > 0 \ . \tag{43}$$

Exactly at the Hopf bifurcation point,

$$-2\varepsilon_1 - \varepsilon_2\varepsilon_3 = 0 \tag{44}$$

Consequently, from Eqns. (43) and (44), if $\varepsilon_2 > 3$ then $\beta_2 > 0$, and the

periodic solutions are unstable. If $\varepsilon_2 < 3$, it follows that $\beta_2 < 0$ and the periodic solutions are stable.

Case 3 ($db_2b_3 < 0$, $\varepsilon_1 < 0$):

Hopf bifurcation is possible only at the minimum $\hat{x}_{s1} = 0$. Here

$$\hat{\beta}_2 = \frac{3d^3b_2^3b_3^3}{4\varepsilon_3^2} < 0 \ . \tag{45}$$

Clearly in this case stable periodic solutions are expected to appear as Hopf bifurcation occurs.

Case 4 ($db_2b_3 < 0$, $\varepsilon_1 > 0$):

No Hopf bifurcation is possible since there are no minima.

Summarizing, stable periodic solutions are possible close to a minimum if

$$\text{i.} \quad db_2b_3 > 0,\ \varepsilon_1 > 0, 0 < \varepsilon_2 < 3, -2\varepsilon_1 - \varepsilon_2\varepsilon_3 < 0 \tag{46.1}$$

or

$$\text{ii.} \quad db_2b_3 < 0,\ \varepsilon_1 < 0,\ \varepsilon_1 - \varepsilon_2\varepsilon_3 < 0 \ . \tag{46.2}$$

In each case, the possibilities for global behavior may be discerned by examining the shape of the potential well. Thus in Case 1, the particle will go either to the minimum or to infinity. If the minimum is unstable then the "friction" is everywhere negative so that the "particle" will gain energy as it moves and will go to infinity.

In Case 2 the situation is even more interesting. If the two minima are stable, depending on the starting point, the particle will go to one. If the minima are unstable, the particle can oscillate about one of them, move from basin to basin in an oscillatory fashion or go to infinity. In Case 3, depending on the starting

point, the particle will go either to the minimum if it is stable or go to infinity. If the minimum is unstable, the particle will perform either stable oscillations close to the minimum or again go to infinity. Finally, in Case 4, the particle will definitely go to infinity.

For this problem, although conditions (i) and (ii) of the theory for existence and stability are met in all four cases, condition (iii) is violated in Cases 3 and 4, whereas condition (iv) is violated in Cases 1 and 2.

The conditions for F_1 bifurcation for this problem are

$$\varepsilon_1 = \varepsilon_2 = 0 \,. \tag{47}$$

On perturbing parameters ε_1 and ε_2 from zero, all the different possibilities portrayed in Fig. 4 are locally obtained, with the minima being stable or unstable. This situation is summarized in Fig. 5. In regions I and II, zero is the only steady state. In region I, the steady state is stable whereas in region II it is unstable with unstable periodic solutions appearing to the left of line (a). In regions III and IV, there are three steady states. In region III the two nonzero steady states are stable whereas in region IV all three steady states are unstable and stable periodic solutions exist close to the nonzero steady states.

CONCLUSIONS AND DISCUSSION

The theory for particles moving in a potential well has been used successfully to obtain important information and insight of the nonlinear dynamics for chemical systems of dimensionality three that are reducible by affine transformation to the companion normal form and have constant negative divergence. After the definition of a potential function, a full analogy between the motion of a particle in a potential well and the three-dimensional system of O.D.E's was observed. Steady states correspond to turning points of the potential function,

D_1 and F_1 bifurcations are reflected by a change in the structure of the potential function as the turning point becomes an inflection point.

Hopf bifurcation can be effected without changing the structure of the potential well and corresponds to vanishing of the "friction" at a minimum of the potential function. Using the theory of Hassard et al. [9], an explicit formula for the characteristic exponent was obtained, thus enabling easy determination of the stability of the Hopf-induced limit cycles. In special cases, a theorem due to Liénard may be useful to establish the existence of globally stable periodic solutions.

This treatise, however, indicates another important point. A system which is three-dimensional is seen by a limiting process to behave essentially as a two-dimensional system. This process of reducing the system dimensionality retains all the local features of the original system. Thus the approximation of the three-dimensional system by a two-dimensional system is valid locally even for smaller positive b. For infinitesimal positive b, the system is a perturbed Hamiltonian system and may then behave as three-dimensional. Consequently, the domain of validity of the two-dimensional approximation depends on the value of the divergence b. The same procedure of reducing the system dimensionality may be generalized for systems of any dimensionality if they are reducible to the companion normal form and possess constant negative divergence.

Using the developed theory, the dynamics of an enzymatic reaction system were analyzed completely. In each case, five parameter combinations, i.e. θ, db_2b_3, ε_1, ε_2 and ε_3, influence the dynamics. The conditions to be satisfied by system parameters for different dynamic behaviors were obtained explicitly. The different possibilities of global dynamic behavior were easily visualized exploiting the "particle" motion analog in an easily obtained one-dimensional

potential field.

Nomenclature

A: Matrix in system 2.

$A(x)$: Function defined by Eqn. (7).

b: Positive constant in system (3).

$\hat{b}$: $-\varepsilon_3$.

b_2, b_3: Parameters in system (24).

d_i: Parameters in system (24).

D_1, F_1, G_1: Types of bifurcation.

$f(x)$: Function in system (3).

$\hat{F}(x), \hat{f}(x), \hat{g}(x)$: Functions in Eqn. (15):

f_1, f_2, f_3: Functions in systems (1) and (3).

$\hat{f}$: Functions in Eqn. (28).

g: Function in system (2).

S_i: Eigenvalues given in Eqn. (17).

s: Variable in characteristic Eqn. (18).

$\hat{s}$: Variable in Eqn. (26).

$u(x)$: Potential function defined in Eqn. (14).

$\hat{U}(\hat{x})$: Potential function given by Eqn. (33) for the quadratic case and Eqn. (39) for the cubic case.

x, y, z: Variables in systems (1) and (3).

$\hat{x}, \hat{y}, \hat{z}$: Variables in system (24).

$\mathbf{z}_e$: Steady-state value of system (29).

$\mathbf{x}^{ss}$: Steady-state value of x (system 13).

$\mathbf{x}, \mathbf{y}$: Vectors in system (2).

GREEK SYMBOLS

$\alpha(x)$: Function in system (3).

$\hat{\alpha}(x)$: Function in Eqn. (29).

β_2: See Eqn. (21).

$\hat{\beta}_2$: See Eqn. (35) for the quadratic case and Eqns. (41, (42) and (45) for the cubic case.

Δ: See Eqn. (32).

ε_i: Parameters defined by Eqns. (25).

θ: Parameter in system (24).

ρ: Power in system (24).

τ: Dummy variables in Eqn. (6).

Subscript

o: Initial value.

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APPENDIX: DERIVATION OF A FORMULA FOR THE CHARACTERISTIC EXPONENT

The algorithm for determining the leading term in the asymptotic expansion for the characteristic exponent is given by Hassard et al. (Hassard R. D., Kazarinoff N. D. and Wan Y. H., "Theory and Applications of Hopf Bifurcation", Cambridge University Press, 1981). For two-dimensional systems, this algorithm is the following:

1. Select the bifurcation parameter ν. Let

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x};\nu) \quad (\mathbf{x} \in R^n) \tag{1}$$

2. Locate $\mathbf{x}^0(\nu)$, the stationary point of interest. Calculate the eigenvalues of the Jacobian matrix

$$A(\nu) = \left\{ \frac{\partial f_i}{\partial x_j}(\mathbf{x}(\nu);\nu) \quad (i,j = 1,2) \right\} \tag{2}$$

3. Find a value ν_c such that $\mathrm{Re}(\lambda_1) = 0$. If (a) λ_1 and λ_2 are a conjugate pair for ν in an open interval including ν_c, (b) $\mathrm{Re}\,\lambda_1'(\nu_c) \neq 0$ and (c) $\mathrm{Im}\,\lambda_1(\nu_c) \neq 0$, then a Hopf bifucation occurs.

4. If $A(\nu_c)$ is in the form

$$\begin{bmatrix} 0 & -\omega_c \\ \omega_c & 0 \end{bmatrix} \tag{3}$$

where $\omega_c = \mathrm{Im}\lambda_1(\nu_c) > 0$, let $P = I$ the identity matrix and go to step 5. Otherwise, form matrix P as follows. Let $P = (\mathrm{Re}\mathbf{v}_1, -\mathrm{Im}\mathbf{v}_1)$ where $\mathbf{v}_1$ is the eigenvector of $A(\nu_c)$ corresponding to $\lambda_1(\nu_c) = i\omega_c$. Normalize $\mathbf{v}_1$ so that its first nonvanishing component is 1.

5. Perform the change of variables

$$\mathbf{x} = \mathbf{x}^0(\nu_c) + P\mathbf{y} \tag{4}$$

and let $\dot{\mathbf{y}} = \mathbf{F}(\mathbf{y})$ denote the system for $\mathbf{y}$. The Jacobian matrix $\partial F^i / \partial y_j\,(0)$ (i,j =

1,2) will have the canonical form

$$\frac{\partial F}{\partial y}(0) = \begin{bmatrix} 0 & -\omega_c \\ \omega_c & 0 \end{bmatrix} \tag{5}$$

6. Calculate the following quantities, all to be evaluated at $\nu = \nu_c$, y=0

$$g_{11} = \frac{1}{4}\left[\frac{\partial^2 F^1}{\partial y_1^2} + \frac{\partial^2 F^1}{\partial y_2^2} + i\left[\frac{\partial^2 F^2}{\partial y_1^2} + \frac{\partial^2 F^2}{\partial y_2^2}\right]\right] \tag{6.1}$$

$$g_{02} = \frac{1}{4}\left[\frac{\partial^2 F^1}{\partial y_1^2} - \frac{\partial^2 F^1}{\partial y_2^2} - 2\frac{\partial^2 F^2}{\partial y_1 \partial y_2} + i\left[\frac{\partial^2 F^2}{\partial y_1^2} - \frac{\partial^2 F^2}{\partial y_2^2} + 2\frac{\partial^2 F^1}{\partial y_1 \partial y_2}\right]\right] \tag{6.2}$$

$$g_{20} = \frac{1}{4}\left[\frac{\partial^2 F^1}{\partial y_1^2} - \frac{\partial^2 F^1}{\partial y_2^2} + 2\frac{\partial^2 F^2}{\partial y_1 \partial y_2} + i\left[\frac{\partial^2 F^2}{\partial y_1^2} - \frac{\partial^2 F^2}{\partial y_2^2} + 2\frac{\partial^2 F^1}{\partial y_1 \partial y_2}\right]\right] \tag{6.3}$$

$$g_{21} = \frac{1}{8}\left[\frac{\partial^3 F^1}{\partial y_1^3} + \frac{\partial^3 F^1}{\partial y_1 \partial y_2^2} + \frac{\partial^3 F^2}{\partial y_1^2 \partial y_2} + \frac{\partial^3 F^2}{\partial y_2^3}\right.$$

$$\left. + i\left[\frac{\partial^3 F^2}{\partial y_1^3} + \frac{\partial^3 F^2}{\partial y_1 \partial y_2^2} - \frac{\partial^3 F^1}{\partial y_1^2 \partial y_2} - \frac{\partial^3 F^1}{\partial y_2^3}\right]\right] \tag{6.4}$$

7. Let

$$C_1(0) = \frac{i}{2\omega_c}\left[g_{20}g_{11} - 2|g_{11}|^2 - \frac{1}{3}|g_{02}|^2\right] + \frac{g_{21}}{2} . \tag{7}$$

Then

$$\beta_2 = 2\mathrm{Re}C_1(0) . \tag{8}$$

System (13) of Chapter 6 may be written as:

$$\dot{x}_1 = x_2 \tag{9.1}$$

$$\dot{x}_2 = \frac{b\alpha(x_1) - f'(x_1)}{b^2}x_2 + \frac{f(x_1)}{b} \tag{9.2}$$

Select b as the bifurcation parameter. At Hopf bifurcation,

$$f'(x_1^H) - b\alpha(x_1^H) = 0 \tag{10}$$

The Jacobian of system (9) is

$$\begin{bmatrix} 0 & 1 \\ \dfrac{f'(x_1^{\#})}{b} & 0 \end{bmatrix} \tag{11}$$

with eigenvalues $\lambda_{1,2} = \pm i\omega_c$ where $\omega_c = -\alpha(x_1^{\#})$. Then

$$v_1 = \begin{bmatrix} 1 \\ i\omega_c \end{bmatrix} \tag{12}$$

Consequently,

$$P_1 = \begin{bmatrix} 1 & 0 \\ 0 & \alpha(x_1^{\#}) \end{bmatrix} \tag{13}$$

Let

$$y_1 = x_1 - x_1^{\#}(b_c) \tag{14.1}$$

$$y_2 = \frac{x_2}{\alpha(x_1^{\#}(b_c))} \tag{14.2}$$

where b_c is the critical value of the bifurcation parameter b for which condition (10) holds. The change of variables gives the new system

$$\dot{y}_1 = \alpha(x_1^{\circ}(b_c))y_2 \tag{15.1}$$

$$\dot{y}_2 = \left[\frac{\alpha(x_1^{\circ}(b_c) + y_1)}{b} - \frac{f'(x_1^{\circ}(b_c) + y_1)}{b^2}\right] y_2 + \frac{f(x_1^{\circ}(b_c) + y_1)}{b\alpha(x_1^{\circ}(b_c))} . \tag{15.2}$$

Then

$$\frac{\partial F(0)}{\partial y} =$$

$$= \begin{bmatrix} 0 & \alpha(x_1^{\circ}(b_c)) \\ \dfrac{b\alpha'(x_1^{\circ}(b_c)) - f''(x_1^{\circ}(b_c))y_2}{b^2} + \dfrac{f'(x_1^{\circ}(b_c))}{b\alpha(x_1^{\circ}(b_c))} & \dfrac{b\alpha(x_1^{\circ}(b_c)) - f'(x_1^{\circ}(b_c))}{b^2} \end{bmatrix} \tag{16}$$

Evaluating the g_{ij} at zero, one gets

$$g_{11} = \frac{1}{4}\left[\frac{if''(x_i^*(b_c))}{b\alpha(x_i^*(b_c))}\right] \tag{17.1}$$

$$g_{02} = \frac{1}{4}\left[-2\,\frac{b\alpha'(x_i^*(b_c)) - f''(x_i^*(b_c))}{b^2} + i\,\frac{f''(x_i^*(b_c))}{b\alpha(x_i^*(b_c))}\right] \tag{17.2}$$

$$g_{20} = \frac{1}{4}\left[2\,\frac{b\alpha'(x_i^*(b_c)) - f''(x_i^*(b_c))}{b^2} + i\,\frac{f''(x_i^*(b_c))}{b\alpha(x_i^*(b_c))}\right] \tag{17.3}$$

$$g_{21} = \frac{1}{8}\left[\frac{b\alpha''(x_i^*(b_c)) - f'''(x_i^*(b_c))}{b^2} + i\,\frac{f'''(x_i^*(b_c))}{b\alpha(x_i^*(b_c))}\right] \tag{17.4}$$

Substituting in the expression for $C_1(0)$ (Eqn. 7),

$$C_1(0) = \left\{\frac{(b\alpha' - f'')f''}{16b^3\alpha^2} + \frac{b\alpha'' - f'''}{16b^2}\right\} + i\left\{\frac{5}{48}\,\frac{f''}{b^2\alpha^3} + \frac{b\alpha' - f''}{24b^4} + \frac{f'''}{16b\alpha}\right\} \tag{18}$$

where the arguments of f, α and their derivatives have been omitted for simplicity. Consequently,

$$\beta_2 = 2\mathrm{Re}(C_1(0)) = \frac{(b\alpha' - f'')f''}{8b^3\alpha^2} + \frac{b\alpha'' - f'''}{8b^2}. \tag{19}$$

Figure Captions

Figure 1: Potential function for the feedback-regulated enzyme reaction sequence. Here $2\theta db_2b_3 + \varepsilon_1 < 0$. If the opposite is true, both turning points are negative.

Figure 2: Steady states in the quadratic case ($\rho = 2$) as a function of ε_1 ($\theta db_2b_3 < 0$).

Figure 3: Functions in the quadratic case ($\rho = 2$).

Figure 4: Potential function in the cubic case ($\rho = 3$, $\theta = 0$).

Figure 5: Regions for different steady-state and dynamic behavior of the enzymatic reaction system close to an F_1 bifurcation ($\varepsilon_3 < 0$).

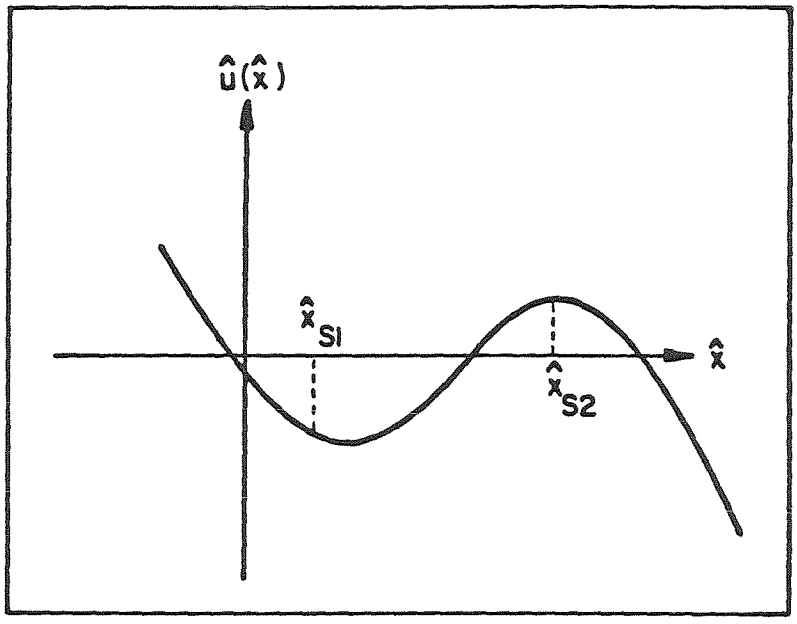

FIGURE 1

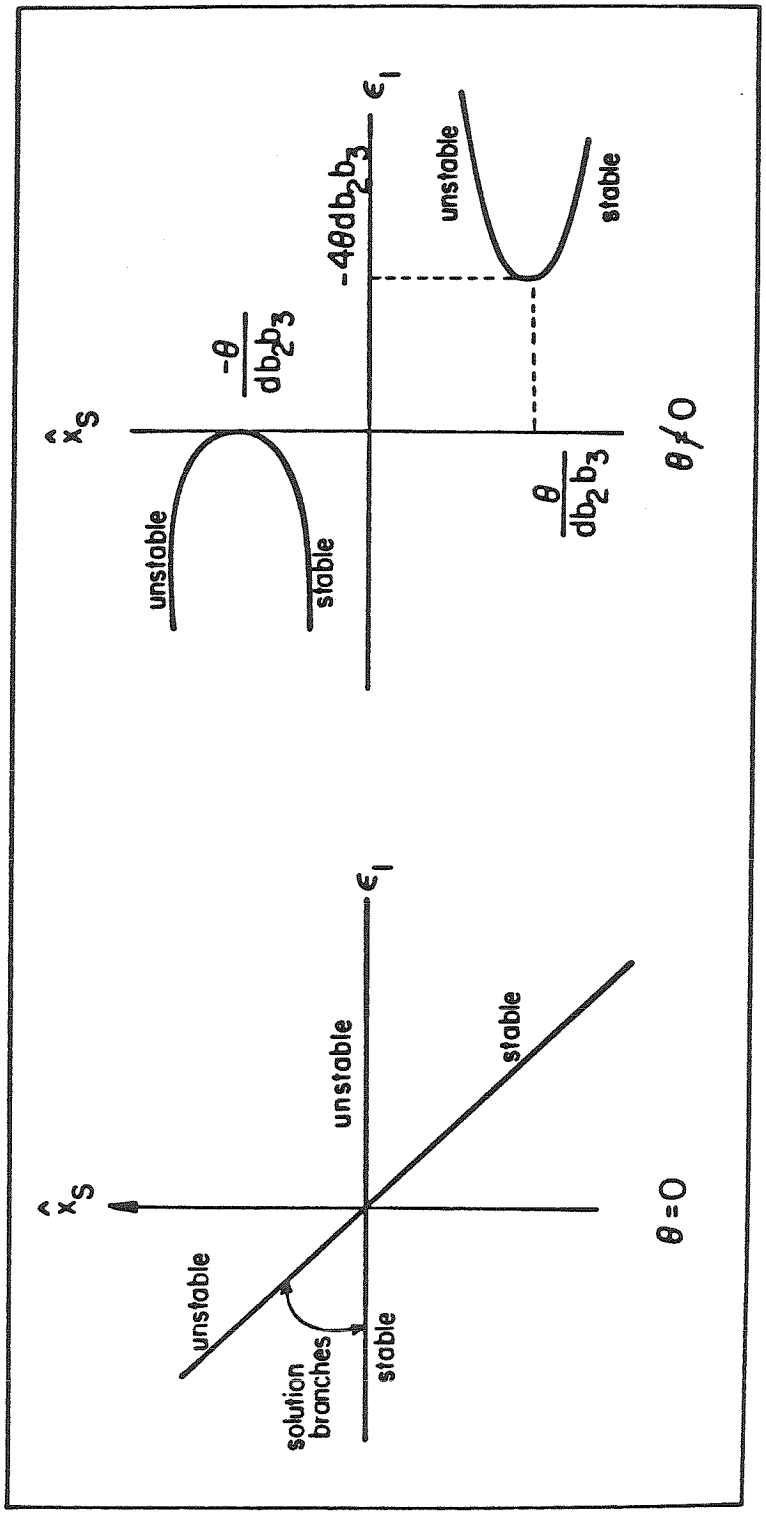
$\hat{x}_s$
ϵ_1
unstable
stable
$\frac{-\theta}{db_2b_3}$
$-4\theta db_2b_3$
$\frac{\theta}{db_2b_3}$
$\theta \neq 0$
$\hat{x}_s$
ϵ_1
unstable
stable
unstable
stable
solution branches
$\theta = 0$

Figure 2

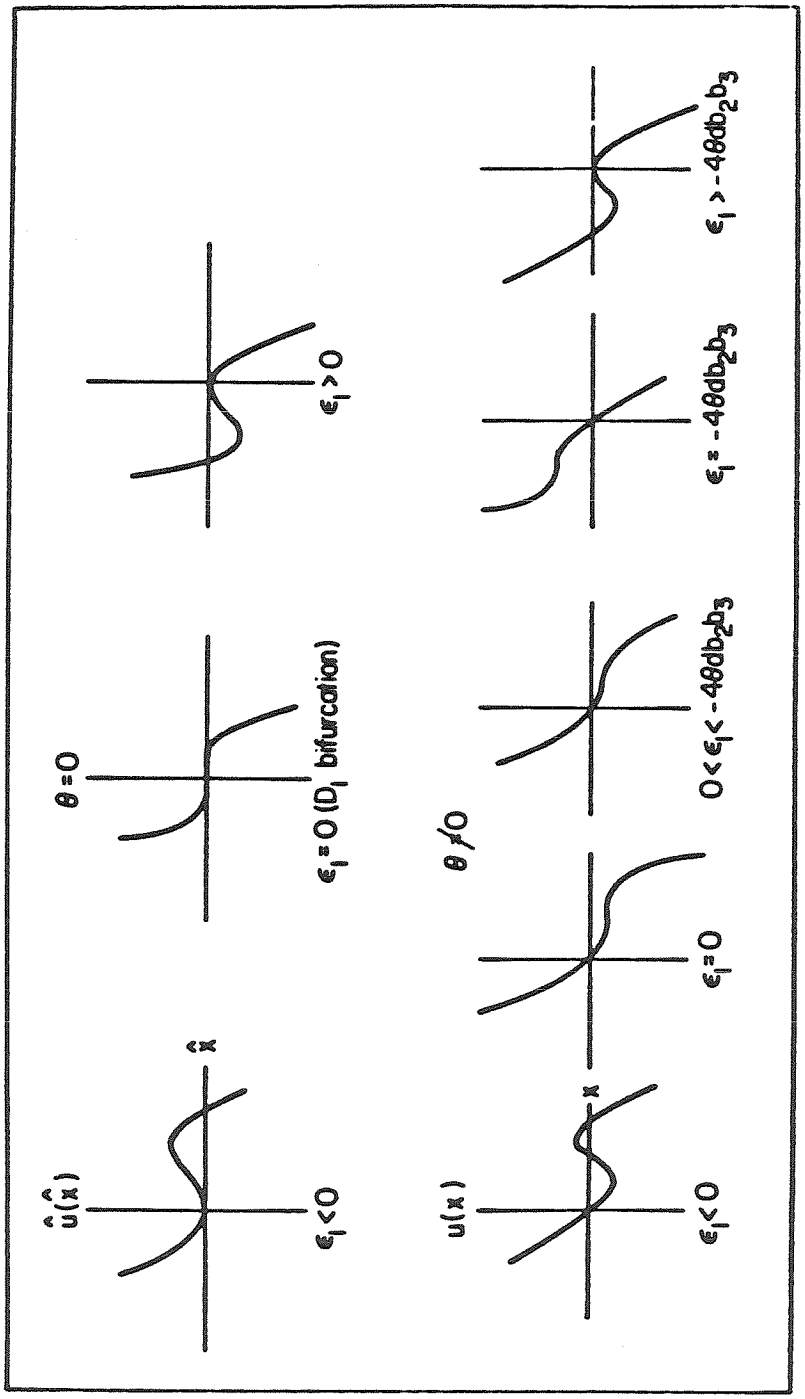
$\hat{u}(\hat{x})$
$\hat{x}$
$\epsilon_1 < 0$
$\theta = 0$
$\epsilon_1 = 0$ (D_1 bifurcation)
$\epsilon_1 > 0$
$u(x)$
x
$\epsilon_1 < 0$
$\theta \neq 0$
$\epsilon_1 = 0$
$0 < \epsilon_1 < -4\theta db_2 b_3$
$\epsilon_1 = -4\theta db_2 b_3$
$\epsilon_1 > -4\theta db_2 b_3$

Figure 3

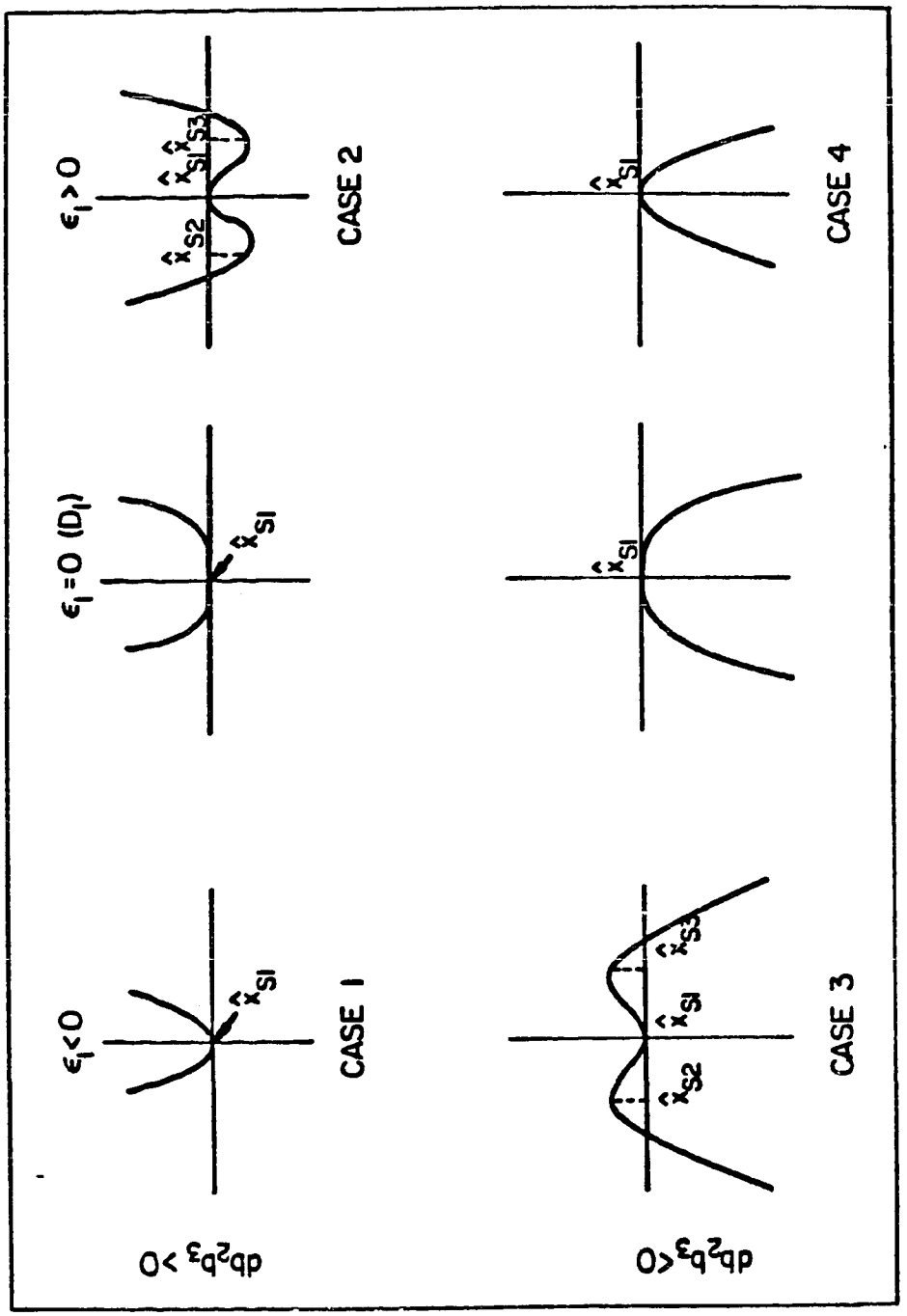
$db_2b_3 > 0$
$db_2b_3 < 0$
$\epsilon_1 < 0$
$\epsilon_1 = 0\ (D_1)$
$\epsilon_1 > 0$
$\hat{x}_{S1}$
$\hat{x}_{S2}$
$\hat{x}_{S3}$
CASE 1
CASE 2
CASE 3
CASE 4

Figure 4

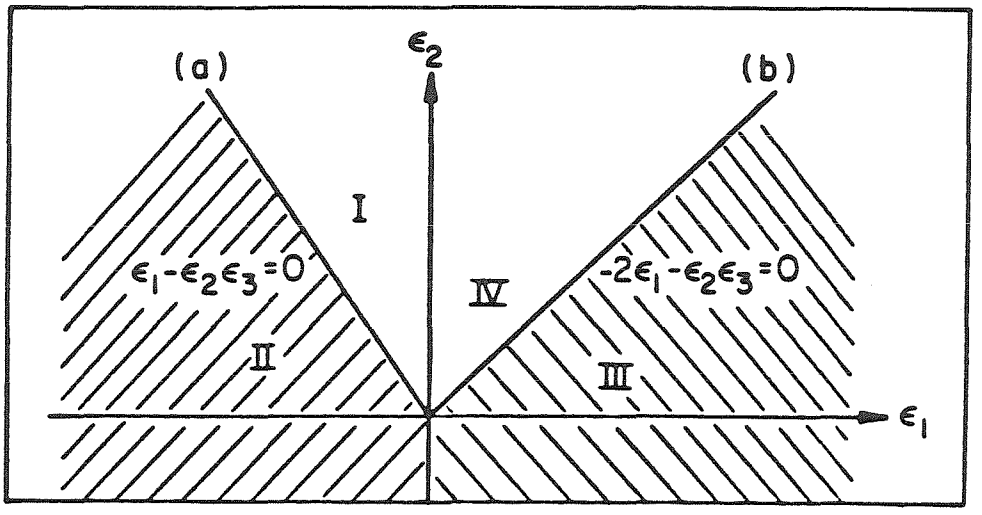
(a)
ϵ_2
(b)
I
$\epsilon_1-\epsilon_2\epsilon_3=0$
IV
$-2\epsilon_1-\epsilon_2\epsilon_3=0$
II
III
ϵ_1

Figure 5

CONCLUSIONS

Methods of bifurcation theory and nonlinear dynamics have been used to develop a general strategy for sensitive modeling and analysis of nonlinear chemical processes.

Modification of the dynamics of chemical reaction systems by multivariable feedback control schemes has been demonstrated to be an invaluable tool for obtaining nonlinear dynamic models of global validity. When steady-state and transient response measurements are unable to discriminate between rival kinetic models, the feedback method provides a clear means of distinction. A general model parameter identification scheme was developed. Complete stratification of the feedback parameter space (decrement diagram) was developed, organizing the study of the possible bifurcations. Feedback produces different types of bifurcations, the most common being D_1 bifurcation usually accompanied by steady-state bifurcation and D_2 (Hopf) giving rise to oscillatory behavior.

The method of Newton Polyhedra proved particularly useful in analyzing feedback-induced steady-state bifurcations when reduction to a single algebraic equation is impossible or impractical. Furthermore, it provides much simpler polynomial forms that are locally equivalent to the original complicated systems.

The number of feedback parameters required to force a system to a certain bifurcational structure was determined using two methods, one based on the characteristic equation of the Jacobian and one based on Arnold's theory of versal families of matrices. The theory of normal forms was used to demonstrate that systems at bifurcation are even locally nonlinear as far as dynamic behavior is concerned. The possible types of dynamic behavior close to a bifurcation are given by the much simpler normal form of the original system.

The reduction of an arbitrary nonlinear system to normal form being particularly difficult, a general class of dynamic systems (those involving a single nonlinearity) was identified that is reducible by an affine transformation to the companion normal form with distinctive advantages for the study of the steady-state and eigenvalue structures. This normal form in the two- and three-dimensional cases is shown to be equivalent to the classical F_1 and G_1 normal forms, respectively.

Systems reducible by affine transformation to the G_1 normal form with constant negative divergence are shown to have a mechanical analog of particle motion in a potential field. This analogy provides special insights into the system dynamics, and conclusions regarding possible global dynamic behavior are drawn.

Using the methods that were developed, important conclusions were drawn regarding the dynamic and steady-state characteristics of numerous chemical reaction systems such as isothermal catalytic nitrous oxide decomposition in a CSTR, isothermal reaction between two adsorbed species in a catalytic CSTR, parallel reactions of arbitrary order in a nonisothermal CSTR, consecutive-competitive reactions in a CSTR, coupling of two isothermal oscillating autocatalytic CSTR's enzymatic feedback reaction systems and another catalytic reaction system. The methods and approaches that were developed should be extremely useful in analyzing the nonlinear dynamics of chemical reactor systems and in obtaining good nonlinear dynamic models for control and optimization.